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PREPARATION AND EVALUATION OF ACTIVATED CARBON PRODUCED FROM MUNICIPAL REFUSE

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FOREWORD

An important objective of the U.S. Environmental Protection Agency is to aid the development of economic and efficient solid waste management practices. The production of increased quantities of materials resistant to biological and chemical degradation has made the disposal of solid wastes increasingly difficult. Changing patterns in the national social structure have affected the quantity of solid wastes as well as the quality and composition. Occurring simultaneously with waste production is the consumption of resources and energy needed to convert raw materials into wastes. Obviously, evergy and resources are not unlimited - and neither is the ability of the environment to withstand the continued abuse resulting from production, consumption and disposal of wastes.

It is the goal of this project to investigate partially the possibility of reducing the impact of wastes on the environment by using an integrated solid waste and wastewater disposal system. The approach is to study specific aspects of a series of processes which can convert the by-products of solid waste disposal into adsorbents which can, in turn, be used for the physical-chemical treatment of wastewaters. It is hoped that such a system will minimize the solid waste disposal problem, improve the level of waste water treatment and permit some recyclable refuse components to be more easily separated. Thus, the ultimate goal is to reduce the quantity of wastes which must be assimilated by the environment and possibly, provide an alternative means of supplying the increasing demands for some natural resources.

A. W. Breidenbach Ph.D., Director
National Environmental Research Center - Cincinnati

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ABSTRACT

Activated carbons were produced from municipal refuse. The carbons were characterized by determining the methylene blue number, iodine number, phenol number, COD adsorptive capacity (municipal sewage), ash content, apparent density, surface area and pore size distribution. The rate of COD adsorption, rate of settling and leachate characteristics were also investigated.

Municipal refuse was shredded, air classified, pyrolyzed, air classified (a second time), activated and ground. A number of different activation schemes were used; the most effective was steam at 910 C without the use of catalysts. Activation was accomplished as a batch process in a fluidized bed.

The refuse activated carbon was compared with Aqua Nuchar A, Calgon BL and Darco M for selected adsorptive properties. Results of several COD adsorption tests indicate that the refuse activated carbon is comparable to Aqua Nuchar A for COD removal.

The approximate yield of activated carbon was ten percent, or 200 lbs per ton of raw refuse. The cost of producing the activated carbon was 5.5 cents per pound when pyrolysis costs are included and 0.93 cents per pound when pyrolysis costs are not included.

CHAPTER 1

INTRODUCTION

Waste disposal has traditionally been accomplished by the cheapest and most convenient method with little or no concern for degradation of the environment. The most common methods are land disposal and burning. Land disposal, aside from polluting other phases of the environment, is rapidly consuming more land than is available for that purpose, while burning, unless conducted with expensive control systems, causes air pollution. Society can no longer afford the 'cheapest' disposal methods; new means must be developed. Ideally, waste disposal should have a minimum impact on the environment and a low total cost. If 'total' cost and environmental impact are interpreted to include the disposal, pollutional and resource consumption costs, the most logical means of disposal is some form of recycling.

The recycle concept is a good one, but, as of 1972, recycling has not been successful on a large scale. Recycling of solid wastes has been orientated to obtaining the more valuable and easily separable refuse components and supplying them to existing markets; the markets are, unfortunately, buyers' markets with minimal prices. In view of low prices and high transportation costs for salvaged items, recycling operations are, at most, marginal. A new approach to recycling is needed: one that is concerned with the creation and improvement of markets for refuse components, and with the development of new methods of processing refuse to supply these markets. Expanded markets would give recycling operations stability and, possibly, reduce

the separation and handling costs of salvage. New processing methods may be used to convert some of the unmarketable refuse components into potentially valuable products that could create a market for themselves. A new system of recycling must be developed which creates and supplies new markets as well as supplying and improving existing ones.

The purpose of this study is to investigate the conversion of a portion of municipal refuse that is currently unmarketable into a product that may create a market for itself. The idea of producing activated carbon from refuse is intriguing, because the activated carbon can be used for treating wastewaters to a high degree. Solid wastes can be used to purify liquid wastes. The potential for a significant reduction in the impact of solid and liquid wastes on the environment exists if such a conversion is possible and, perhaps more important, economical.

The Scope and Organization of This Report

The use of pyrolysis as a disposal method for municipal refuse is currently being considered by both commerical and government groups. Pyrolysis can effectively reduce municipal refuse to a stable and odor-free residue composed of carbonaceous material and refuse inerts (glass, metal, ash, etc.). The carbonaceous portion of the pyrolysis residue is a char which can be converted into an activated carbon. The principal objective of this research project was to investigate the conversion of municipal refuse into an activated carbon by subjecting the refuse to pyrolysis and activation processes.

Refuse activated carbons were prepared by a number of activation processes and the resulting carbons were evaluated for adsorptive capacity. The adsorption of organics from sewage is considered to be the intended use of the refuse activated carbon, and, as a result, the COD adsorptive capacity is considered as the most important carbon evaluation parameter. Refuse carbons were also tested for methylene blue, iodine and phenol adsorptive capacity. The adsorptive capacity of the refuse carbons has been compared with three commercially available activated carbons.

In the arrangement of chapters, Chapter 4 dealing specifically with the experimental results of pyrolysis and activation studies is preceded by a chapter on the background and theory of activation (Chapter 2). The specific methods and procedures used in the evaluation of the refuse and commercial carbons are given in Chapter 3. An economic evaluation of the activation process and a typical wastewater treatment scheme using activated carbon is reported in Chapter 5. Chapter 6 contains a summary of the main results of the research, a brief statement of the significance of the findings with respect to wastewater treatment, and, finally, some suggestions for further research on activated carbons produced from municipal refuse.

CHAPTER 2

BACKGROUND AND THEORY OF ACTIVATION

I. BRIEF HISTORY AND DESCRIPTION OF CARBON ADSORBENTS

The use of carbon adsorbents can be traced back to ancient times. Early Greeks used charcoal as a medicine to treat sores, presumably to adsorb infectious fluids. Marco Polo reported that the 13th Century Chinese used charcoal to refine sugar [1]. In the middle ages, water barrels for use on ships were charred on the inside to help keep the water palatable.

In recent times, adsorbents more efficient than charcoal were developed to meet man's needs. Bone char was discovered in 1811 by Figuier and was used extensively for sugar refining soon after. The first 'activated' carbon may have been discovered by Bussy in 1822 [2]. Bussy heated blood with potash and produced an adsorbent 20 to 50 times as good as bone char. Maleziewz proposed the use of steam during the carbonization of peat in 1856, and in 1863, Lee prepared a deodorizing carbon by the action of steam and air on peat [2]. In 1900 and 1901, Ostrejko patented the first 'chemical' and 'physical' activation processes; adsorbents produced under the Ostrejko patents soon came into widespread use throughout Europe. With the advent of World War I, gas mask adsorbents stimulated American interest in activated carbon.

The term 'activated carbon' is used to describe a family of substances that are, basically, modified chars. Chars are the high carbon content solid residues that result from the pyrolysis of carbonaceous materials. The modification process, which is known as activation, is used to increase

the adsorptive capacity of the char. Activated carbons do not have a unique formula, structure or set of adsorptive properties; activated carbons can be prepared from nearly all carbonaceous materials by any of several activation processes.

The physical properties of activated carbons are different from those of unactivated carbons (chars or primary carbons) [3, 4]. Activated carbons are more crystalline than primary carbons, and have a higher surface area, a lower apparent density, a higher true density, higher pore volumes, and a more extensive system of micro, transitional and macro pores. Surface area is regarded as one of the most significant physical properties of activated carbons; high surface areas are usually associated with a high adsorptive capacity. Surface areas of activated carbons may exceed 1,000 M^2/gm, while primary carbons have surface areas in the range of 40 M^2/gm to 60 M^2/gm.

II. DEFINITION OF ACTIVATION

The term 'activation' is defined as any process which selectively removes the hydrogen or hydrogen rich fractions from a carbonaceous material in such a manner as to produce an open porous residue [5]. The terms 'chemical activation' and 'physical activation' have come into use to describe the two general methods by which activated carbons are produced [6]. Chemical activation is accomplished by pyrolyzing raw carbonaceous materials, like sawdust, that have been impregnated with chemical additives (Figure 2-1). Physical activation is accomplished by contacting primary carbon, the inactive char product of pyrolysis, with suitable solvents or gases under controlled conditions (Figure 2-1).

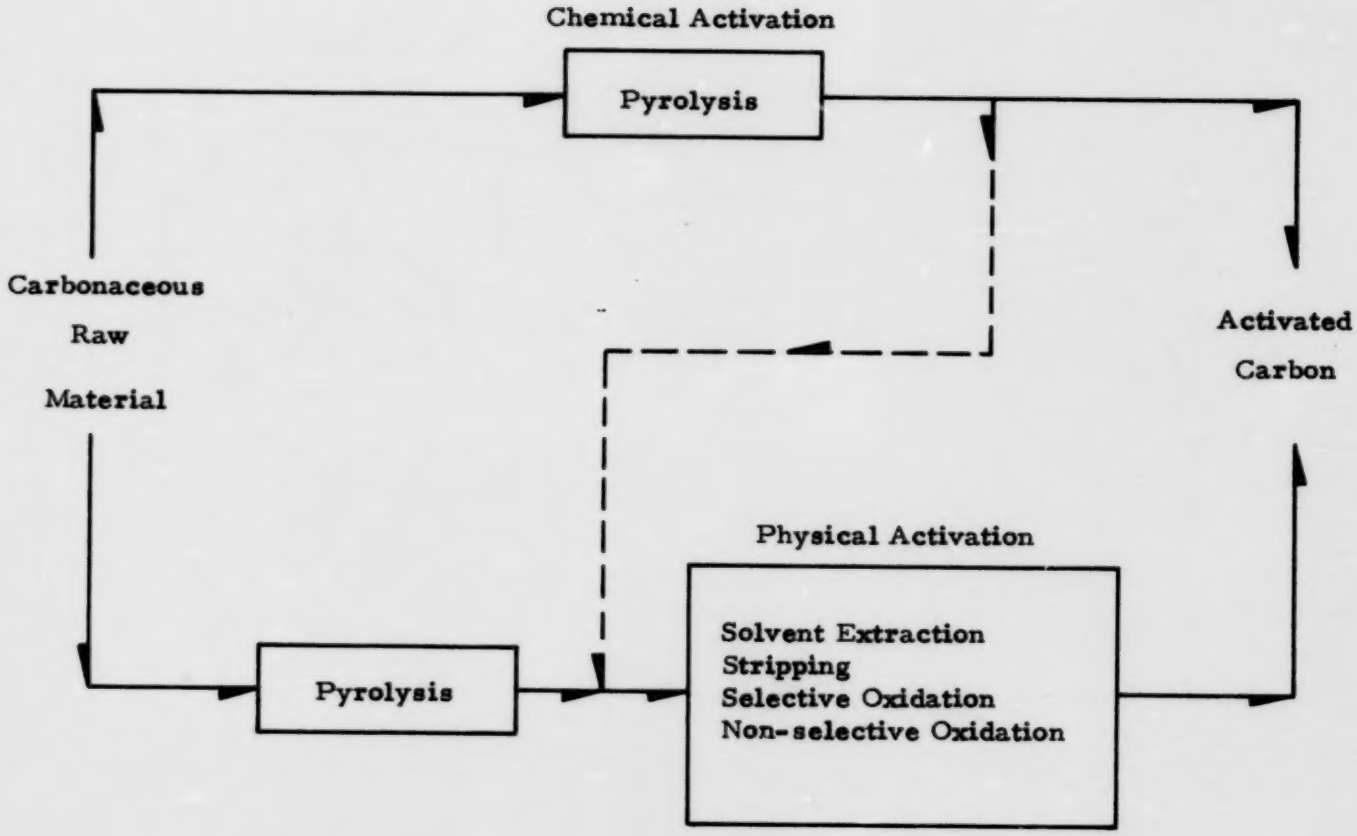

Figure 2-1. Processes used for physical and chemical activation. After Kipling [7].

A combination of the physical and chemical activation processes can be used. Smisek and Cerny [6] state that only certain methods of physical activation can produce carbons with a high adsorptive capacity. In some cases, chemically activated carbons are further activated by physical activation to increase the adsorptive capacity.

III. THE PYROLYSIS PROCESS

The first step in the conversion of raw materials into activated carbons is pyrolysis. Pyrolysis is defined as the decomposition of organic substances by heat [7]. In the absence of oxygen, the products of pyrolysis are gases, tars, oils and char. The tars and oils, when condensed together, are commonly referred to as 'pyroligneous acids'. Char is known as primary carbon, unactivated carbon, pyrolysis residue and several other terms that relate to the starting material (e.g., coke from coal, charcoal from wood, etc.). Depending upon the industry using the process, pyrolysis is referred to as carbonization, coking or distillation.

The chemistry of the pyrolysis process is extremely complicated. The number of specific compounds resulting from the pyrolysis of complex materials like coal and wood is not known, but over 1,000 compounds have been detected in the pyrolysis products of coal [8]. Several investigators [9-11, others] have attempted to trace the decomposition reactions for several materials. Fragmentation (depolymerization, hydrolysis, oxidation, dehydration, decarboxylation) and reformation (pyrogenetic synthesis) of the pyrolysis products makes accurate determination of the decomposition reactions difficult.

The pyrolysis of cellulose was studied by Tang and Bacon [10], who separated the process into four parts based on different temperature ranges. In the range 25 C - 150 C physical desorption of water from the cellulose material occurs. The dehydration of the cellulose unit takes place between 150 C - 240 C. Temperatures in excess of 250 C cause cleavages of the C-O and C-C bonds which break down the cellulosic unit and result in the production of tars, CO_2, H_2O and CO. Finally, at temperatures above 400 C, aromatization (growth of the graphitic crystallites) is initiated. Other researchers agree upon the approximate temperature at which aromatization begins [12, 13]. Bolton et. al. [12] report that between 500 C and 600 C CH_4 production is maximum and at 700 C production of CO and H_2 is maximum. Above 700 C, the gas produced is mainly H_2. C-H bonds apparently break between 500 C and 700 C. Bolton et al. also state that, during aromatization, only carbon combines to form the stable hexagonal pattern (i.e., S and N are excluded), and that other substances are easily detached from it as the volatilization temperature of the particular substance is reached.

The pyrolysis of coal and peat involves a series of fragmentation and reformation reactions that are, in general, similar to those for cellulose. The pyrolysis products are somewhat different in proportion and composition for each substrate used, and the temperatures at which the various compounds are evolved may vary [9, 14, 15].

The composition and quantity of the pyrolysis products depends upon the pyrolyzing atmosphere, the time of pyrolysis, the maximum temperature attained, the pressure, the rate of heating, and the substrate used [9]. Fuchs and Sandhoff [9] state that for coal pyrolysis, the average molecular weight of the volatile intermediate products decreases as the temperature

of pyrolysis increases (this is probably true for materials other than coal). Char yield is reduced by a high rate of heating, and is also reduced as the temperature of pyrolysis is increased; a reduction in char yield results in a subsequent increase in the yields of other pyrolysis products.

IV. PYROLYSIS FOR REFUSE DISPOSAL

The increasing costs of incineration and the scarcity of land for sanitary landfills, coupled with environmental concern, has provided the motivation to investigate pyrolysis as a possible method of treatment prior to ultimate disposal. Although pyrolysis cannot, currently, compete economically with landfills, pyrolysis does appear to be competitive with incineration when air pollution standards are considered. Pyrolysis, like incineration, can effectively reduce the weight and volume of refuse, and pyrolysis residue, like incinerator ash, is stable and odor free.

Typical composition of refuse is shown in Table 2-1. Approximately 75 percent of the refuse is carbonaceous material which can be pyrolyzed to yield gases, tars, oils and char. The end product of refuse pyrolysis is a biologically stable mixture of char and refuse inerts (glass, metal, ash, etc.) called pyrolysis residue. The Landgard system, developed by Monsanto, utilizes the pyrolysis process for disposal and is reported to reduce the volume of refuse by 94 percent after removal of ferrous metals from the pyrolysis residue [16].

One advantage of refuse pyrolysis over other disposal methods is the possibility of resource recovery. Recoverable and potentially valuable refuse by-products include combustible gases, oils, char and a variety of

TABLE 2-1

COMPOSITION OF REFUSE

Component	[21*]	[22]	[23]	[24]	[25]	[26]	Average	
Paper	54.46%	42.0%	55.6%	42-57%	60.0%	48.0%	52%	
Food Wastes	8.50	12.0	11.1		8.5	16.0	11.2	
Wood, Leaves, etc.	9.17	14.4	5.6	10-12	8.0	11.9	9.8	
Plastics	.76	.7	5.6		3.5	2.0	2.5	
Rags	.76	.6		.6-2	.5	1.0	.8	≈75%
Rubber	.38	.3			.4		.4	
Leather	.38	.3			.4		.4	
Paint and Oils	.76	.8			.3		.6	
Dirt and Dust	2.29	4.0			.5		2.3	
Metals	6.85			1.5-8	8.0	8.0		
Glass	7.73	14	16.7	2-15	8.0	6.0	23.6	
Ashes		10		5-19		8.0		
Other	9.05 moisture		5.6 misc.		.5 misc.			

* Refers to References.

specific organic compounds such as acetic acid, acetone, etc. The gases, char and oils (including tars) are all a possible source of energy and can be used for the energy requirements of the pyrolysis process (Figure 2-2). The char, if properly activated, may be a suitable adsorbent for such uses as wastewater treatment. In addition, other resources like ferrous metals are easily separated from pyrolysis residue.

The pyrolysis of municipal refuse has been investigated by several researchers [17-20]. Typical yields of the pyrolysis products from refuse are presented in Table 2-2. A summary of the pyrolysis yields for some refuse components is given in Table 2-3. The variability of the yields in Table 2-2 can be attributed to differences in pyrolysis conditions, differences in refuse composition and alteration of the refuse moisture content by the investigator. For example, the percent yield of char for Sanner et al. [19] would be about 16.3 percent if the refuse was dried prior to pyrolysis (the value in Table 2-2 is 9.3 percent). Yield depends on such parameters as rate of heating, atmosphere, pressure, temperature and total time of pyrolysis.

V. THE ACTIVATION PROCESS

The purpose of this section is to present and summarize some of the theories on activation in order to explain how activated carbon is prepared from the pyrolysis residue of municipal refuse. Some material is included on activation mechanisms to provide a basis for later discussion.

Investigation of the properties and activation mechanisms of activated carbons has been extensive [2-7, 28-38]. Only part of the available

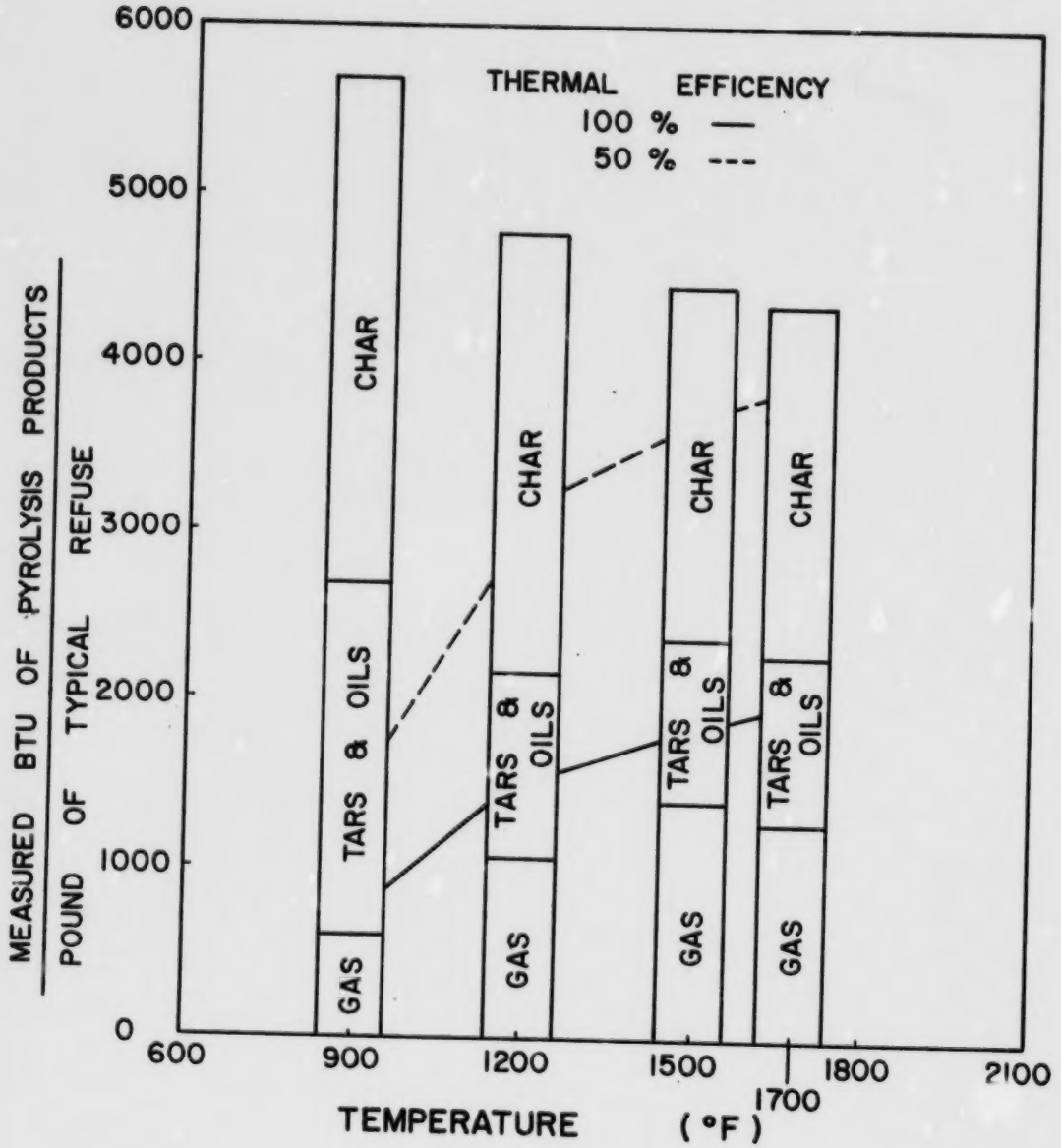

Figure 2-2. Energy of pyrolysis products as function of pyrolysis temperature. Energy required to sustain process plotted as solid and dashed lines. (After Hoffman and Fitz (17)).

TABLE 2-2

PYROLYSIS YIELDS FOR MUNICIPAL REFUSE

(Yields are expressed as the percent weight of refuse)

Investigator →	After Hoffman and Fitz [17]				Sanner [19] et al.	Mallan [27]	Stanford
Pyrolysis Temperature	482 °C 900 °F	648 °C 1200 °F	815 °C 1500 °F	925 °C 1700 °F	900 °C 1652 °F	500 °C 932 °F	680 °C 1257 °F
Char Yield	24.7%	21.8%	17.2%	17.7%	9.3%	35%	32%
Oil and Tar Liquid Yield	61.1	59.2	59.7	58.7	58.6	55	-
Gas Yield	12.3	18.6	23.7	24.3	26.7	10	-
Total	98.1%	99.6%	100.6%	100.7%	94.5%	100%	-
Comments on Refuse:	Moisture ≃ 20%. Glass and Metal Removed.				Moisture ≃ 43%. No Glass and Metal.	Refuse Samples Oven Dried.	Moisture ≃ 30%. Some Glass and Metal Removed.

TABLE 2-3

PYROLYSIS YIELDS OF REFUSE COMPONENTS*

(T = 1500 °F = 815 °C)

Component	Gas	Oil and Tar Liquid	Pyrolysis Residue (Char and Ash)
Rubber	17.29%	46.36%	36.35%
Hardwood Leaf Mixture	22.29	44.14	33.57
White Pine Sawdust	20.41	57.28	22.31
Newspaper	25.82	44.07	30.11
Corrugated Box Paper	20.89	45.98	33.13
Magazine Paper	19.53	36.78	43.69
Lawn Grass	26.15	36.19	37.66
Vegetable Food Waste	27.55	47.39	25.06

* Modified from Kaiser [18].

literature on activated carbon is listed in the references. Additional sources of information are available within the articles, reviews and books cited as references.

The terms 'chemical activation' and 'physical activation' have come into general use and, although neither involves processes that are exclusively chemical or physical in nature, the terminology has been accepted. Each of the methods has advantages and, depending on the expected use of the carbon, one is usually more desirable than the other. Chemical activation, which is favored in Europe, has the advantage of producing an activated carbon in a single operation and gives comparatively high carbon yields. Physical activation, which is more popular in the United States, requires two operations, but has the capability of producing the best adsorbents. In addition, activated carbons can be produced from a larger variety of raw materials when a physical activation process is used (e.g., coal, rubber, graphite, petroleum, coke, etc.).

A. Physical Activation

Physical activation converts char into activated carbon by selective removal of char components. Char components are removed, to varying degrees, by four basic processes: solvent extraction, stripping, selective oxidation and non-selective oxidation. Of the above processes, non-selective oxidation is the most effective.

Chars are composed of elemental carbon, hydrocarbons and ash (inorganic compounds). Chars that are suitable for the production of activated carbons are generally low in ash and hydrocarbons and high in elemental carbon. The ash in char is the result of salts present in the raw material and metal oxides formed during pyrolysis. Ash typically contains K, Na, Mg, Ca, Fe, Al , Cl ,

SO_4, PO_4 and traces of other elements and compounds. The quantity of hydrocarbons in chars is a function of the pyrolysis conditions and can be reduced by increasing the pyrolysis time and/or temperature. Hydrocarbons result from compounds present in the raw material and from substances formed by pyrogenetic synthesis. Hydrocarbon compounds may be chemically or physically bonded to the elemental carbon portion of the char.

The elemental carbon in char is present in two structural forms, noncrystalline and crystalline. The noncrystalline, or amorphous, carbon has a highly disordered structure and is randomly dispersed between the crystalline portions. The crystalline carbon is in the form of hexagonal plateletts which are stacked in nearly parallel layers called elementary graphite crystallites. The layered structure of the crystallites provides an extensive network of pores which, if open and accessible, can contribute a large surface area per unit weight.

The true density of activated carbons approaches that of graphite (a very crystalline form of carbon), and X-ray studies have shown that the elemental carbon in activated carbons is much more crystalline than the elemental carbon in char. The activation process apparently removes hydrocarbons and amorphous carbon from char (thus creating access to the extensive pore structure of the graphitic crystallites) while selectively leaving some of the crystalline carbon.

Selective removal of char components by solvent extraction, stripping or selective oxidation is, generally, not practical for commercial production, but these processes are used for the preparation of specialty carbons. Solvent extraction and stripping at high temperatures with an inert gas can

be used to remove some hydrocarbons (those weakly bonded chemically and physically) from the char, but these processes are not effective in removing any elemental carbon and, probably, none of the strongly bonded hydrocarbons. Selective oxidation can effectively remove hydrocarbons, but has little effect on elemental carbon. Selective oxidation can be used, for example, to produce gas adsorbents of high mechanical strength by contacting sulfur gas with char at temperatures too low for carbon oxidation. Under these conditions, hydrocarbons will oxidize and the elemental carbon (which forms the structural matrix) remains intact. Only the non-selective oxidation process can effectively remove hydrocarbons and elemental carbon.

Non-selective oxidation is accomplished by subjecting the char to an oxidizing atmosphere at high temperatures. The most commonly used gases are steam, carbon dioxide, and air. Sulfur gas, Cl_2, H_2, etc. can also be used, but these gases are of little practical interest. The reactions of carbon with steam and carbon dioxide are endothermic, while the reaction of carbon with oxygen is exothermic (activation with air is very difficult because uncontrolled burning can occur due to the exothermic reaction). Steam and carbon dioxide are used at temperatures in the 700 C to 1,300 C range, while air is used at temperatures from 300 C to 600 C. The basic reactions for steam-carbon and carbon dioxide-carbon oxidation are:

$$C + H_2O = H_2 + CO$$

and

$$C + CO_2 = 2CO$$

respectively. These basic reactions do not take into account the numerous secondary reactions which occur. Reaction rates are determined experimentally and are very sensitive to temperature and catalysts.

Non-selective oxidation can be considered to occur in three steps. Assuming an ash free char, as pictured in Figure 2-3A, the unactivated material is composed of hydrocarbons, amorphous carbon and elementary graphitic crystallites. The first step in the non-selective oxidation process is the oxidation and physical stripping of the hydrocarbons by the oxidizing gas; the resulting carbon is shown in Figure 2-3B. The carbon produced by the first step (Figure 2-3B) is considered to be an activated carbon, and is similar to carbons produced by the solvent extraction, stripping and selective oxidation processes; surface area is greater for this carbon than for char, but the pore network is blocked by amorphous carbon. In the second step (Figure 2-3C), oxidation of the amorphous carbon takes place and an activated carbon with a large percentage of micropores results. The elementary graphitic crystallites remain intact because they are slightly more resistant to oxidation than the amorphous carbon [32]. Continued oxidation, which is the third and final step, results in partial oxidation of the elementary graphitic crystallites; an activated carbon with a wide range of pore sizes and unrestricted pore access is produced (Figure 2-3D). For some adsorbents, as much as 85 percent of the char may be oxidized, or otherwise lost, during the activation process [5]. The amount of char lost during activation is related to the adsorptive capacity of the carbon produced [7].

Catalysts can be used during physical activation to aid in carbon oxidation and to give activated carbons special adsorptive properties. The effect of catalysts on carbon oxidation reactions, which occur during physical activation, have been investigated [30, 39-49, others]. In general, catalysts increase the rates of certain stages of oxidation and permit the use of lower

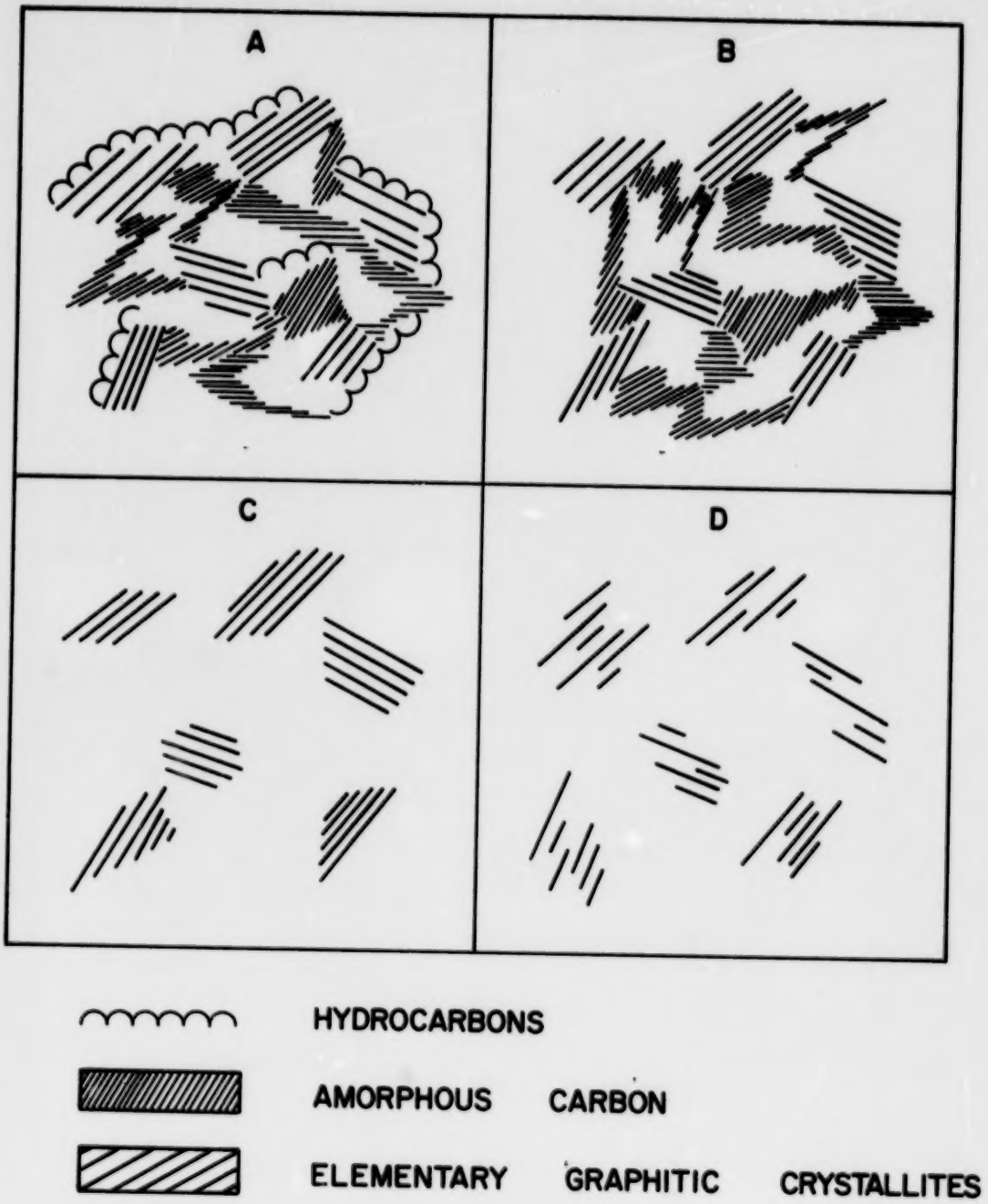

Figure 2-3. Illustration of the selective removal of char components by the activation process.

A-raw char, B-hydrocarbons removed, C-amorphous carbon removed, D-partial removal of graphitic crystallites.

activation temperatures. Selective adsorptive properties can be obtained by the use of catalysts [1, 41] and pore sizes and size distributions can be controlled [41]. The selective adsorptive properties may arise from the controlled pore sizes, from the presence of compounds introduced as catalysts which react chemically with specific adsorbates, or from the catalytic influence on the number and types of functional groups which remain on the crystallites after activation. The mechanism by which pore sizes are controlled is not clearly understood, but there is evidence that some catalysts (e.g., alkali metal ions) actually spread apart the planes of the graphite crystallites to form new pores [4, 45].

B. Chemical Activation

Chemical activation is accomplished by the pyrolysis of chemically treated raw materials. Chemical additives are mixed with carbonaceous materials of recent origin, like sawdust, and kneaded until a homogeneous mass is formed. The homogeneous material is pyrolyzed at 600 C to 700 C and subjected to an extraction process to remove the additive. The resulting material is an activated carbon (similar to Figure 2-3B).

The effects of chemical additives are to catalyze the pyrolysis process, inhibit the formation of tars, increase the char yield and to provide void space within the carbon when the additives are extracted. The catalytic effect of the additives accelerates the pyrolysis process by increasing the rate of dehydration. The mechanism by which tar formation is inhibited is not clearly understood; tars are either dehydrated by the presence of the additive, or they are physically not capable of condensing on the carbon surface because of the presence of the additive. Char yield is increased

by the dehydrating action of the additives; hydrogen and oxygen are expelled from the raw material as water, and, as a result, the hydrocarbon yield is decreased with a consequent increase in char yield. Chemical additives are dehydrating agents and include $ZnCl_2$, K_2S, H_3PO_4, H_2SO_4, NaOH, KOH, $MgCl_2$, $CaCl_2$, and KSCN.

The adsorptive capacity of chemically activated carbons (activity) is related to the degree of impregnation. The degree of impregnation is defined as the weight ratio of the additive to the starting material (on a dry basis). Smisek and Cerny [6] describe a chemical activation process for pine sawdust and $ZnCl_2$ that uses one part sawdust to two parts $ZnCl_2$.

The advantages of the chemical activation process are high carbon yields, single operation pyrolysis-activation and comparatively low temperature requirements. The disadvantages are that further activation is necessary to produce a carbon with a high adsorptive capacity and that additives are not always easily extracted from the activated carbon. In addition, degrees of impregnation on the order of 1:2 would result in material handling problems for large scale production processes.

VI. CONVERSION REFUSE INTO ACTIVATED CARBON

The conversion of carbonaceous raw materials into activated carbons by pyrolysis and physical activation appears to be the most desirable method when municipal refuse is used as the raw material. Pyrolysis, if used as a refuse disposal method, would result in large quantities of char which may be activated by physical activation.

Physically activated carbons have a higher absorptive capacity than those activated chemically, and for a heterogeneous material like refuse, a chemical activation process may not be effective in dehydrating all refuse components (e.g., plastic, rubber, etc.). In addition, the chemical and material handling costs necessary for chemical activation would be enormous in view of the quantity of refuse which must be displosed of annually.

Because of the potential availability of char (if pyrolysis is used as a disposal method) and because of the effectiveness of physical activation, the emphasis of this study is on the production of activated carbon from refuse using pyrolysis and the non-selective oxidation process. A number of catalysts are studied, and the effect of these substances on carbon oxidation and adsorptive capacity has been determined. The objective has been to produce the best COD adsorbent at lowest cost.

CHAPTER 3

METHODS AND PROCEDURES

The values of the parameters used to characterize activated carbons are very sensitive to the methods and procedures used to determine these values. Details of the methods and procedures used in the current study are included to permit others to examine, compare and evaluate these methods.

I. REFUSE PROCESSING

A. Source of Refuse and Method of Processing

All refuse samples were obtained from the Combustion Power Company (CPC) of Palo Alto, California. Refuse is delivered to CPC in 5-ton packer trucks supplied by the City of Palo Alto. Municipal or industrial refuse can be selected. Municipal refuse was used for all pyrolysis-activation work.

The refuse is ground with an Eidal shredder and partially separated with a modified zig-zag air classifier. The material passing through the air classifier (about 85 percent of the raw refuse) was used for the study. The air classified material contains 10-15% inerts (i.e., glass and metal).

1. Moisture Content Determination

The percent moisture of the refuse samples is determined by drying at 103 C for 24 ± 1 hour. Samples of about 300g are placed in shallow pans and weighed to the nearest 0.1g before and after drying. Moisture content is defined as the percent weight loss resulting from the drying.

II. PYROLYSIS

A. Pyrolysis Procedure

Pyrolysis was conducted as a batch process using a modified metal

processing furnace supplied by the Pereny Equipment Company. The furnace is equipped with a stainless steel retort which can be inserted into the preheated furnace. The temperature range of the furnace is 0 C - 950 C and can be controlled to within ± 5 C.

The furnace is equipped with a thermocouple that extends into the retort and both furnace and retort temperatures can be read continuously. The rate of heating of the retort is not controlled directly; the rate is a function of the furnace temperature and the load in the retort.

Refuse samples, placed inside the retort, are inserted into the preheated furnace. Sample size is arbitrary and is generally about 900g. The retort is purged with N_2 at the rate of 2l/min (at STP) during heating and cooling to prevent oxidation of the char.

Pyrolysis is considered complete for the lower temperature batches (500 C and 680 C) when gas production diminishes. For the high temperature (910 C) batches, pyrolysis is considered complete when the desired retort temperature is attained.

Char yield is defined as the percent weight of material remaining after pyrolysis.

III. PROCESSING PYROLYSIS RESIDUE PRIOR TO ACTIVATION

A. Air Classification

Pyrolysis residue was separated with a modified zig-zag air classifier (Figure 3-1). Air classificiation is used to reduce the ash content of the material to be activated.

The pyrolysis residue was passed through a 3/8-inch sieve, prior to entering the air classifier, in order to break up the larger clumps of char.

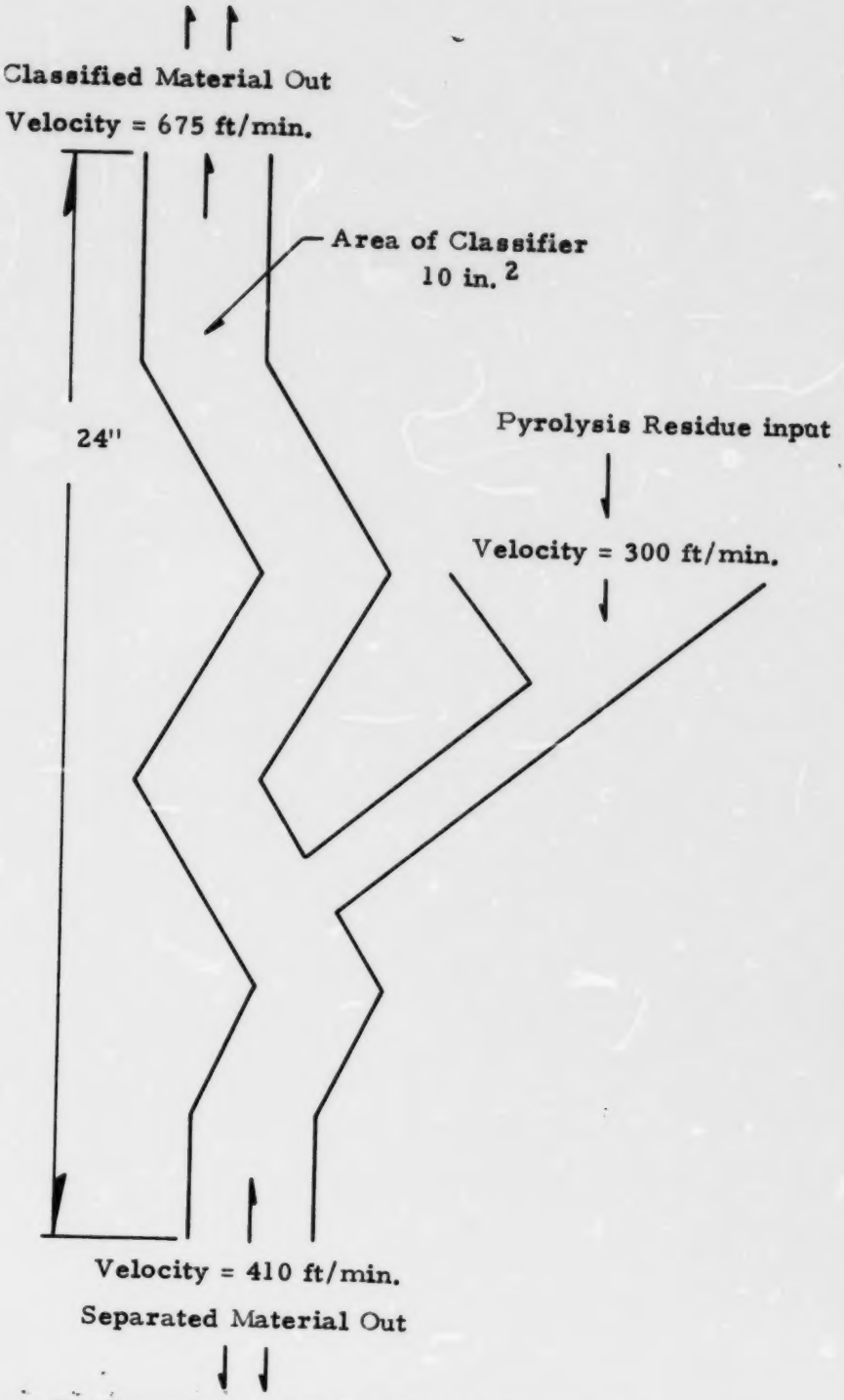

Figure 3-1. Configuration and velocities of the modified zig-zag air classifier used for ash separation.

Air velocities in the classifier were measured with a Cenco anemometer.

B. Application of Catalysts

Char samples are contacted with catalysts by placing the char in boiling deionized water which contains the desired amount of catalyst. The samples are then dried at 103 C for 48 hours.

IV. ACTIVATION

A. Activation Procedure

Activation is accomplished as a batch process with the same furnace and retort used for pyrolysis. The char is placed in a stainless steel activation unit designed to fit inside the retort (Figure 3-2).

The activation unit is brought up to temperature and cooled down in an inert nitrogen atmosphere; the inert atmosphere does not pass through the carbon bed during heating and cooling. During activation, gases pass upward through the carbon bed (Figure 3-2).

The quantity of activating gases is measured either by flow-rate or weight. Air, carbon dioxide and nitrogen are measured with a rotameter. The quantity of steam is determined from the weight loss of the boiling flask used to supply the steam.

The activation time is considered as the time that the activating gases are in contact with the char at the activation temperature. The times required for heating and cooling are not considered as activation time.

V. PROCESSING ACTIVATED CARBONS FOR EVALUATION

A. Grinding

Activated refuse carbons are ground in a one gallon ball mill. The ball mill contains 30 steel balls about three quarters of an inch (3/4'')

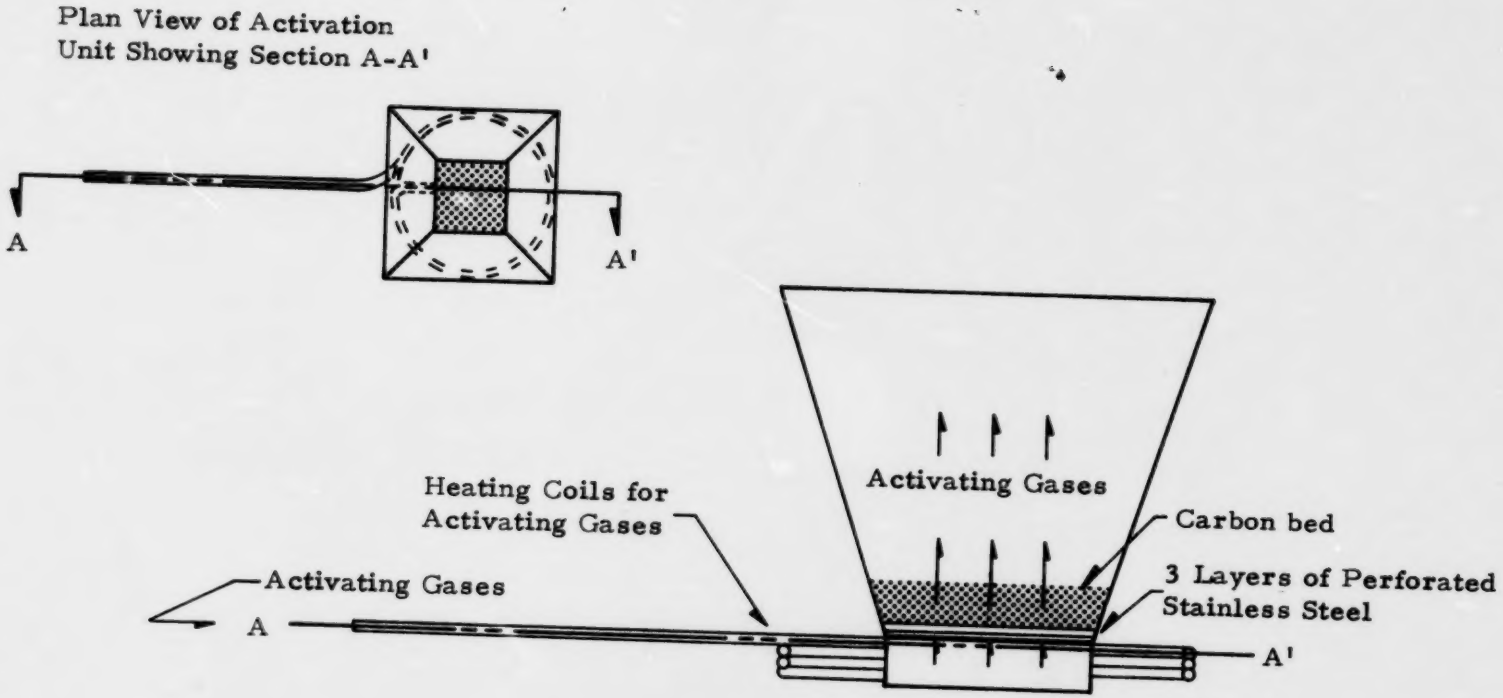

Figure 3-2. Cross section of the activation unit.

in diameter and the mill is shaken on a table shaker at 200 cycles per minute for 8 minutes.

B. Sieving

After grinding, the activated carbon is dry sieved through No. 10 and No. 100 Tyler sieves. The sieves are shaken for 8 minutes at 200 cycles per minute. The portion of the activated carbon passing the No. 100 sieve is characterized.

VI. CARBON CHARACTERIZATION

A. Percent Ash

Percent ash (ash content) is defined as the percent weight of the char that will not volatilize or oxidize in air at a temperature of 600 C for 2 hours.

Sample Sizes Used for Percent Ash Determination

1. Unseparated pyrolysis residue of about 40g (to nearest 0.1g).
2. Air classified pyrolysis residue of about 10g (to nearest 0.0001g).
3. Activated carbon of about 2g (to nearest 0.0001g).

B. Percent Volatile Matter

Percent volatile matter is defined as the percent weight loss of the char which occurs when the char is stripped for 20 minutes with nitrogen (or He) in a fluid bed at a temperature of 910 C.

Samples Size Used for Percent Volatile Matter Determination

1. Air classified pyrolysis residue ca. 40g (to nearest 0.1g).

Note: The activation unit was used to determine percent volatile matter.

C. Percent Carbon

The percent carbon of the pyrolysis residue (char) is defined as the

percent of the char which is not ash or volatile matter. The percent carbon of an activated carbon (assuming 0% water) is defined as 100 percent minus the percent ash. The percent carbon is calculated from ash content and (for char) percent volatile matter.

D. Methylete Blue Number

The methylene blue number (MB No.) is defined as the milligrams of methylene blue adsorbed by one gram of carbon in equilibrium with a solution of methylene blue having a concentration of 1.0 milligram per liter.

1. Special Equipment and Reagents

   a. Spectrophotometer capable of operation at a λ of 665 nm.

   b. Centrifuge which can maintain 10,000 rpm.

   c. Table shaker.

   d. Stock solution of methylene blue having a concentration of 800 mg/1.

2. Procedure

   a. Prepare a working solution of methylene blue having a concentration of 80 mg/1.

   b. Prepare standards from the working solution to calibrate the spectrophotometer. Use 0.5 mg/1, 1.0 mg/1, 2.0 mg/1, 3.0 mg/1 and 4.0 mg/1; plot calibration curve of absorbance versus concentration.

   c. Carefully weight out carbon samples to the nearest 0.0001g and place in dry 250 ml Erlenmeyer flash with rubber stoppers. The size of the carbon samples is dependent on the activity of the carbon to be tested. Table 3-1 gives the approximate dosages for carbons having MB No.'s from 60-325. Use three samples for each carbon tested.

TABLE 3-1

RANGE OF CARBON DOSES TO BE USED FOR DETERMINATION OF METHYLENE BLUE NUMBER

Approximate Methylene Blue Number of the Carbon to be Tested	The carbon doses (mg) to be used per 100 ml of Methylene Blue working solution with a concentration of 80 mg/l. Three carbon samples are used for each MB No. determination.		
	Sample 1	Sample 2	Sample 3
60	128.0 mg	132.0 mg	136.0 mg
80	96.0	100.0	104.0
100	77.0	80.0	83.0
125	61.0	64.0	67.0
150	51.0	53.0	55.0
175	43.5	45.0	46.5
200	38.5	40.0	41.5
225	34.5	35.5	36.5
250	30.5	31.5	32.5
275	28.0	29.0	30.0
300	25.5	26.5	27.5
325	23.5	24.5	25.5

d. Add 100 ml of the methylene blue working solution (80 mg/1, 25 C) to each of the carbon samples.

e. Mix on a table shaker for 30 minutes at a rate of ca. 200 cycles per minute.

f. After shaking, centrifuge the samples at 10,000 RPM for 10 minutes. Carefully pipette off the supernatant.

g. Determine the concentration of methylene blue in the supernatant using the spectrophotometer.

h. Determination of MB No.

Use the Langmuir isotherm to determine the MB No. graphically; plot X/M versus C_s and note the value of X/M when C_s = 1.0 mg/1. $X = C_o - C_s$, where C_o is the original adsorbate concentration (mg/1) and C_s is the equilibrium concentration (mg/1); M is the carbon dose in equilibrium with the adsorbate and is expressed in g/1. MB No. = X/M when C_s = 1.0 mg/1.

3. Notes on Procedure

This procedure has been developed to determine the MB No. of powdered activated carbons relative to one another. To accurately determine the MB No. of a powdered activated carbon, the temperature of the working solution should be closely controlled (at 25 C), zinc free methylene blue should be used and the carbon should be ground so that 90 percent will pass a 325 mesh sieve [50,51].

The concentration of methylene blue in the working solution can be arbitrarily set at a higher or lower value. When larger carbon sample sizes are desired, as in the case of carbons with high methylene blue adsorptive capacity, the concentration of methylene blue in the working solution can be increased.

In some cases, the centrifuge will not remove all the carbon from solution and filtration must be used. Methylene blue may adsorb on the filter and corrections will be required.

E. Iodine Number

The iodine number (I No.) is defined as the milligrams of iodine adsorbed by one gram of carbon when the iodine concentration of the residual filtrate is 0.02 N (2.54 g/1).

1. Special Equipment and Reagents

a. 5 percent HC1. To 550 ml of deionized H_2O add 70 ml of reagent grade concentrated HC1.

b. 0.025 N $K_2Cr_2O_7$ - Ref. [52], p. 478.

c. 0.01 N $Na_2S_2O_3$ Ref. [52], p. 475

d. KI - Reagent Grade.

e. 1 + 9 H_2SO_4. Add one part concentrated H_2SO_4 to 9 parts H_2O, by volume.

f. Starch Solution - Ref. [52], p. 478.

g. No. 5 Whatman filter paper, 18.5 cm. diameter.

h. Iodine solution. Dissolve 19.1g of reagent grade KI and 12.7g of reagent grade iodine in 25 ml of deionized H_2O. When the iodine has dissolved, dilute to one liter.

2. Procedure

a. Standardize the $Na_2S_2O_3$ - Ref. [52], p. 478-479.

b. Standardize the Iodine Solution:

i. To a 250 ml Erlenmeyer flask add 100 ml of deionized H_2O and 10 ml of 5 percent HC1.

ii. Using a safety bulb, pipette 10.0 ml of I solution into the 250 ml Erlenmeyer.

iii. Titrate with $Na_2S_2O_3$ using starch as an indicator.

Add the starch after the solution is pale yellow in color.

iv. Calculte the N and g/1 of the I solution.

c. Carefully weight out carbon samples to the nearest 0.0001g and place in dry 250 ml Erlenmeyer flasks with rubber stoppers. The size of the carbon samples is dependent on the activity of the carbon to be tested. Table 3-2 gives the approximate dosages for carbons having I No.'s from 200 to 1200. Use three samples for each carbon tested.

d. Add 10 ml of 5 percent HCl to the carbon samples and bring to a boil for 30 seconds.

e. Allow the carbon samples to cool to room temperature and add 100 ml of iodine solution.

f. Shake vigorously for 30 seconds and immediately pour the entire contents of the flask on the No. 5 Whatman filter.

g. Discard the first 25 ml of filtrate.

h. Dilute 50 ml of filtrate to 100 ml with deionized H_2O and titrate with $Na_2S_2O_3$ using starch as an indicator.

i. Determine the g/1 of iodine in the filtrate.

j. Determination of I No.

Use the Langmuir isotherm to determine the iodine number graphically. Plot X/M versus C_s and note the value of X/M when C_s = 2.54 g/1. I No. = X/M when C_s = 2.54 g/1. X, M and C_s are defined under MB No.

3. Notes and Procedure

This procedure has been developed to determine the iodine number of powdered activated carbons relative to one another. To accurately

TABLE 3-2

RANGE OF CARBON DOSES TO BE USED FOR DETERMINATION OF IODINE NUMBER.

Approximate Iodine Number of the Carbon to be Tested.	The carbon doses (g) to be used per 100 ml of iodine working solution having an approximate concentration of 12.5 g/l. Three carbon samples are used for each I. No. determination.		
	Sample 1	Sample 2	Sample 3
200	4.500 g	5.000 g	5.500 g
300	3.000	3.300	3.600
400	2.250	2.500	2.750
500	1.800	2.000	2.200
600	1.500	1.700	1.900
700	1.300	1.250	1.500
800	1.150	1.250	1.350
900	1.000	1.100	1.200
1000	0.900	1.000	1.000
1100	0.820	0.900	0.980
1200	0.750	0.800	0.850

determine the iodine number, the carbon should be ground so that 90 percent will pass a 325 mesh sieve [53-55].

When preparing the iodine solution, it is important to dissolve all of the iodine crystals and KI in the 25 ml of deionized H_2O before diluting to 1 liter.

F. Phenol Number

The phenol number (P No.) is defined as the milligrams of phenol adsorbed by one gram of carbon in equilibrium with a solution of phenol having a concentration of 1.0 mg/1.

1. Special Equipment and Reagents

   a. Spectrophotometer capable of operation at a λ of 271 nm and capable of accommodating at least 4.0 cm cells to get the required sensitivity.

   b. Millipore filter apparatus with 0.45 μm filter pads.

   c. Phenol stock solution - 1,000 mg/1.

   d. Table shaker.

2. Procedure

   a. Prepare a phenol working solution having a concetration of 20 mg/1. Dilute 20.00 ml of stock solution to 1.000 liter.

   b. Prepare standards from the working solution to calibrate the spectrophotometer. Use 0.5 mg/1, 1.0 mg/1, 2.0 mg/1, 3.0 mg/1, and 5.0 mg/1; plot calibration curve of absorbance vs. concentration.

   c. Carefully weight out carbon samples to the nearest 0.0001g and place in dry 250 ml Erlenmeyer flasks with rubber stoppers. The size of the carbon samples is dependent on the activity

of the carbons to be tested. Table 3-3 gives the approximate dosages for carbons having phenol numbers from 10 to 30. Use four samples for each carbon tested.

d. Add 100 ml of phenol working solution (20 mg/1) tc the carbon samples. The temperature of the phenol solution should be 25 C.

e. Mix on a table shaker for 30 minutes at a rate of ca. 200 cycles per minutes.

f. After shaking, filter the samples with a 0.45 μm millipore filter.

g. Using the spectrophotometer, determine the phenol concentration of the filtrate.

h. Determination of P No.

Use the Langmuir isotherm to determine P No. graphically. Plot X/M versus C_s and note the value of X/M when C_s = 1.0 mg/1. Phenol Number = X/M when C_s = 1.0 mg/1. X, M and C_s are defined under MB No.

3. Notes on Procedure

The stock solution must be refrigerated and should not be kept more than 2 weeks; bio-oxidation of the phenol may occur.

When preparing the stock solution, phenol crystals must be weighed out quickly. Solid phenol crystals change weight rapidly when exposed to the atmosphere.

G. COD Correlation Factor

For activated carbons of similar adsorptive capacity, the COD correlation factor (COD c.f.) is defined as the ratio of the amount of COD adsorbed by a

TABLE 3-3

RANGE OF CARBON DOSES TO BE USED FOR DETERMINATION OF PHENOL NUMBER

Approximate Phenol Number of the Carbon to be Tested	The carbon doses (mg) to be used per 100 ml of phenol working solution with a concentration of 20 mg/l. Four carbon samples are used for each P No. determination.			
	Sample 1	Sample 2	Sample 3	Sample 4
10	140	160	180	200
20	80	90	100	110
30	50	60	70	80

specific weight of a standard carbon to the amount of COD adsorbed by the same weight of the carbon being tested. Generally, the COD c.f. is determined by taking an average of the ratios of $(C_o - C_s)_{\underline{\text{standard carbon}}}$ to $(C_o - C_s)_{\underline{\text{test carbon}}}$ at carbon doses of 400 mg/1, 800 mg/1, and 1,200 mg/1.

For COD adsorption evaluation of primary carbons and poor quality activated carbons, the COD c.f. is defined as the average ratio of

$\tau_{\underline{\text{standard carbon}}}$ $\left(\tau = (C_o - C_s)/M\right)$ to the $\tau_{\underline{\text{test carbon}}}$ at several C_s values. The values of C_s used are arbitrary and depend upon the effluent used; generally, a range of C_s values is selected which encompasses linear or parallel portions of the adsorption isotherms. X, M, and C_s are defined under MB No.

Aqua Nuchar A is used as the standard carbon for all COD c.f. evaluations.

Note: TOC correlation factor is determined in the same manner.

1. Special Equipment and Reagents

   a. COD apparatus and reagents – Ref. [52], p. 495. (Use 0.125 N $K_2Cr_2O_7$, 0.05 N Fe $(NH_4)_2(SO_4)_2$ and 4 drops of Ferroin indicator).

   b. Millipore filter apparatus with 0.45 μm filter pads.

   c. Table shaker.

2. Procedure

   a. Weigh out samples (40 mg, 100 mg, 160 mg and 240 mg) of the standard carbon and the carbon to be evaluated. Place

samples in clean and dry 500 ml Erlenmeyer flasks with rubber stoppers.

b. Thoroughly mix the sewage effluent to be tested. Use an osterizer type mixer and a mixing time of 5 minutes.

c. Add 200 ml of the mixed effluent to the carbon samples and shake for 30 minutes at 200 cycles per minute.

d. After 30 minutes of shaking, filter the samples with the 0.45 μm millipore filter.

e. Filter a sample of the mixed effluent which has not been contacted with the carbon.

f. Determine the COD of all the filtrates.

g. Calculation of COD c.f.

i. Plot the concentration of the filtrate (C_s) versus the carbon dose for each of the carbons tested.

ii. Determine the amount of COD adsorbed ($C_o - C_s$) at carbon doses of 400 mg/1, 800 mg/1 and 1,200 mg/1 for each of the carbons.

iii. Divide ($C_o - C_s$) standard carbon by ($C_o - C_s$) test carbon at carbon doses of 400 mg/1, 800 mg/1 and 1,200 mg/1; the average of these three values will be the COD c.f. for the test carbon.

3. Notes on Procedure

The COD apparatus must be very clean for consistent results. The determination of low COD values is very sensitive to contamination from dust, algae in rinse water, etc. The apparatus may be cleaned by

boiling an acid-dichromate mixture in the flasks and using the reflux columns as they would be used in the COD test.

A stronger dichromate solution (0.25 N) may be used for filtered effluents with COD'S greater than 250 mg/1.

H. Surface Area and Pore Size Distribution

Surface area and pore size distribution are determined with a Model 2100 Orr Surface Area and Pore Volume Analyzer. Nitrogen adsorption at 77 K and the B.E.T. equation are used to determine the surface area and supply the data needed to compute the pore size distribution.

I. Apparent Density

The apparent density is defined as the weight of char per unit volume expressed in grams per milliliter.

1. Procedure

a. Weight 10.0g of carbon and place in a dry 100 ml graduate cylinder.

b. Bounce the bottom of the cylinder on a rubber stopper until there is no settling after 2 minutes of continuous bouncing.

c. Record the volume of the carbon when it becomes constant.

d. Apparent density = (10.0g)/(Carbon volume) where the carbon volume is the volume after settling.

J. Rate of COD Adsorption

1. Special Equipment and Reagents

a. COD apparatus and reagents. Ref. [52], p. 495 (and/or TOC carbonaceous analyzer).

b. Millipore filter apparatus with 0.45 μm filter pads.

c. Table shaker.

2. Procedure

a. Weight out 4.00g of the carbon to be tested and place in a clean dry 10 liter bottle.

b. Thoroughly mix the sewage to be tested. Use an osterizer type mixer and a mixing time of 5 minutes.

c. Filter a sample of the mixed effluent immediately before going on with Step d.

d. Add 4.00 liters of the mixed effluent to the carbon and mix vigorously to wet the carbon.

e. Shake at ca. 200 cycles per minute.

f. Withdraw 50 ml samples, as rapidly as possible, after 2 minutes, 5 minutes, 10 minutes, 20 minutes, and 45 minutes. Filter the samples immediately.

g. Determine COD and/or TOC of samples as rapidly as possible after filtering.

h. Plot COD concentration in the filtrate versus time of contact.

3. Notes on the Procedure

To accurately determine rate of adsorption of COD, a control sewage sample (without carbon) should be shaken along with the rate sample to note the extent of bio-oxidation which occurs during the 45 minute contact period. The reduction in COD of the control, which occurs during the contact period, can be determined by direct COD measurement. The difference between the initial COD (at time 0 minutes) and the COD of the control at some time, t, is added to the COD of the rate sample at the corresponding time, t.

K. Settling Tests

1. Special Equipment and Reagents

a. Multiple paddle stirrer.

b. Turbidimeter.

2. Procedure

a. Weight out a series of 1.00 gram samples and place in 250 ml Erlenmeyer flasks with rubber stoppers.

b. Measure out 1.0 liter of sewage effluent and add ca. 100 ml to the carbon sample. Add the remainder of the sewage (ca. 900 ml) to a 2 liter beaker. Shake the carbon flask vigorously to wet the carbon and add the flask contents to the 2 liter beaker containing the remainder of the sewage.

c. Stir the carbon-sewage mixture at 60 RPM for 10 minutes before adding the coagulant.

d. Add the coagulant in the appropriate range of doses.

e. Determine the initial turbidity of the raw effluent.

f. Stir the sewage, carbon and coagulant mixture for 30 minutes at 60 RPM.

g. Record the turbidity of the settled samples 10 minutes, 20 minutes and 30 minutes after stirring is stopped.

h. Plot turbidity versus time with the coagulant done as a parameter.

L. Leachate Characterization

1. Special Equipment and Reagents

a. Conductivity cell.

b. Flame photometer.

c. Table shaker.

d. Millipore filter apparatus with 0.45 μm filter pads.

2. Procedure

a. Weigh out 1.000g of carbon and place in a liter volumetric flask.

b. Fill to 1.00 liter with deionized water and shake for 24 hours at 200 cycles per minute at room temperature.

c. Filter with the 0.45 μm millipore filter and evaluate the filtrate for Na, Hardness, pH, Alkalinity, Conductivity and Dissolved Solids.

Use procedures in [52] for all of the above measurements.

CHAPTER 4

STATEMENT AND DISCUSSION OF EXPERIMENTAL RESULTS

I. REFUSE USED AS THE STARTING MATERIAL

A. Nature and Composition of the Refuse

Palo Alto municipal refuse, which is shredded and air classified, consists mainly of volatile refuse components. The composition of the classified refuse is given in Table 4-1. Moisture content of the classified refuse is about 30 percent (Table 4-2).

The higher density components of shredded refuse (glass, metal, etc.) are small in size (<1/4'' dia.), while pieces of paper and other low density components may be several inches across. Classified refuse has the general appearance and texture of damp, dirty cotton.

Air classification separates out about 15 percent of the raw shredded refuse; the separated portion consists mainly of glass and metal. The classified refuse, which was used for the study, represents about 85 percent of the raw refuse. The composition of the raw refuse used for the study is in general agreement with refuse compositions given in Table 2-1.

II. PYROLYSIS STUDIES

A. Char Yield

Char yield is defined as the percent, by weight, of the refuse which remains as char residue after pyrolysis. Average char yields for each pyrolysis series are given in Table 4-2. The average char yield for separated Palo Alto refuse is 32 percent for a pyrolysis temperature of

TABLE 4-1

THE APPROXIMATE COMPOSITION OF THE AIR CLASSIFIED MUNICIPAL REFUSE USED FOR PREPARING THE ACTIVATED CARBONS.

Refuse Component	Stanford University Analysis (%)	Combustion Power Co. Analysis (%)	Average Composition (%)	Calculated Average Composition Before Drying (%)
Moisture	0%	0%	0%	30%
Paper	74	60	67	47
Wood	5	12	8	5.5
Fabric	1	2	1	0.5
Plastic	2	2	2	1.5
Inerts, Lint and Dust	18	26	22	15
Total:	100%	102%	100%	99.5%

TABLE 4-2

AVERAGE CHAR YIELDS FOR EACH SERIES OF PYROLYSIS BATCHES

Pyrolysis Samples in Each Series	Temperature of Pyrolysis (°C)	Average Time of Pyrolysis (minutes)	Average Percent H_2O in Separated Refuse (%)	Average Char Yield of Refuse (%)	Calculated Average Char Yield of Dry Refuse (%)	Percent of Raw Refuse Separated by Air Classifier Before Pyrolysis (%)
1P-7P	680 °C	57 min.	27%	31%	41%	17%
9P-19P	680	57	26	33	45	17
20P-26P	680	55	29	31	44	7
27P-35P	680	52	13	35	41	12.5
37P-39P	510	115	31	32	45	10-15
40P-41P	680	76	31	30	43	10-15
42P-44P	910	135	31	26	36	10-15

680 C and a pyrolysis time of 59 minutes.

B. Effect of Pyrolysis Temperature on Char Yield

Similar refuse samples were pyrolyzed at 510 C, 680 C, and 910 C to study the effect of pyrolysis temperature on char yield (Figure 4-1). For the refuse sample used, the char yield ranged from 32% to 26% for pyrolysis temperatures of 510 C, 680 C, and 910 C. Char yields obtained by other investigators are given in Table 2-2.

C. Rate of Temperature Increase During Pyrolysis

The rate of retort heating is not controlled and is a function of the temperature at which the furnace is operating. Retort temperature is plotted as a function of time in Figure 4-2.

Rate of heating is nearly constant for each of the pyrolysis temperatures used. Because the rate is constant, the rate of heating is not considered to be a variable in the char production process.

The rate of temperature increase during pyrolysis affects the char yield and is reported to affect the crystal structure of the carbon in the char [56, 57]. Since char yield and crystal structure may ultimately affect refuse activated carbon quantity and quality, respectively, the rate of temperature increase is reported.

III. AIR CLASSIFICATION OF PYROLYSIS RESIDUE

Air classification reduced the ash content of the pyrolysis residue by an average of 30.5 percent. The ash content of unclassified char is ca. 62 percent while the classified char has an ash content of ca. 43 percent. The results of separation by air classification for five different chars are shown in Figure 4-3. The separated material is about 90% ash.

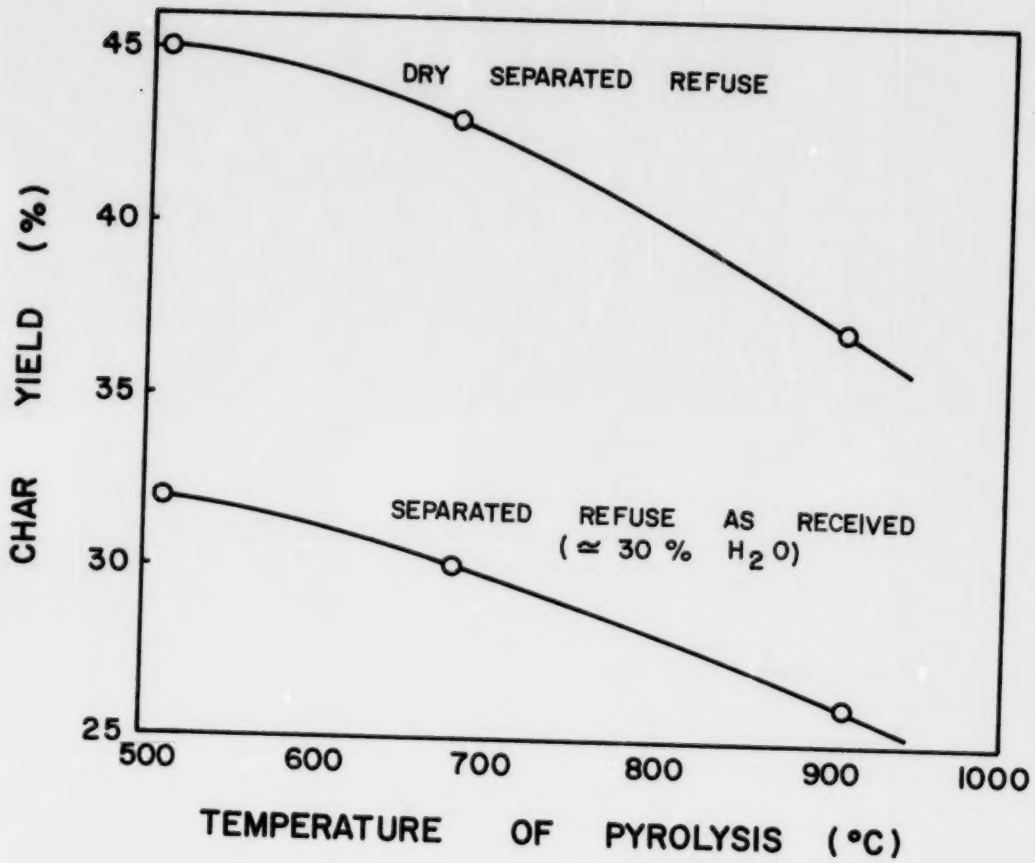

Figure 4-1. Effect of temperature on char yield for separated Palo Alto Municipal refuse.

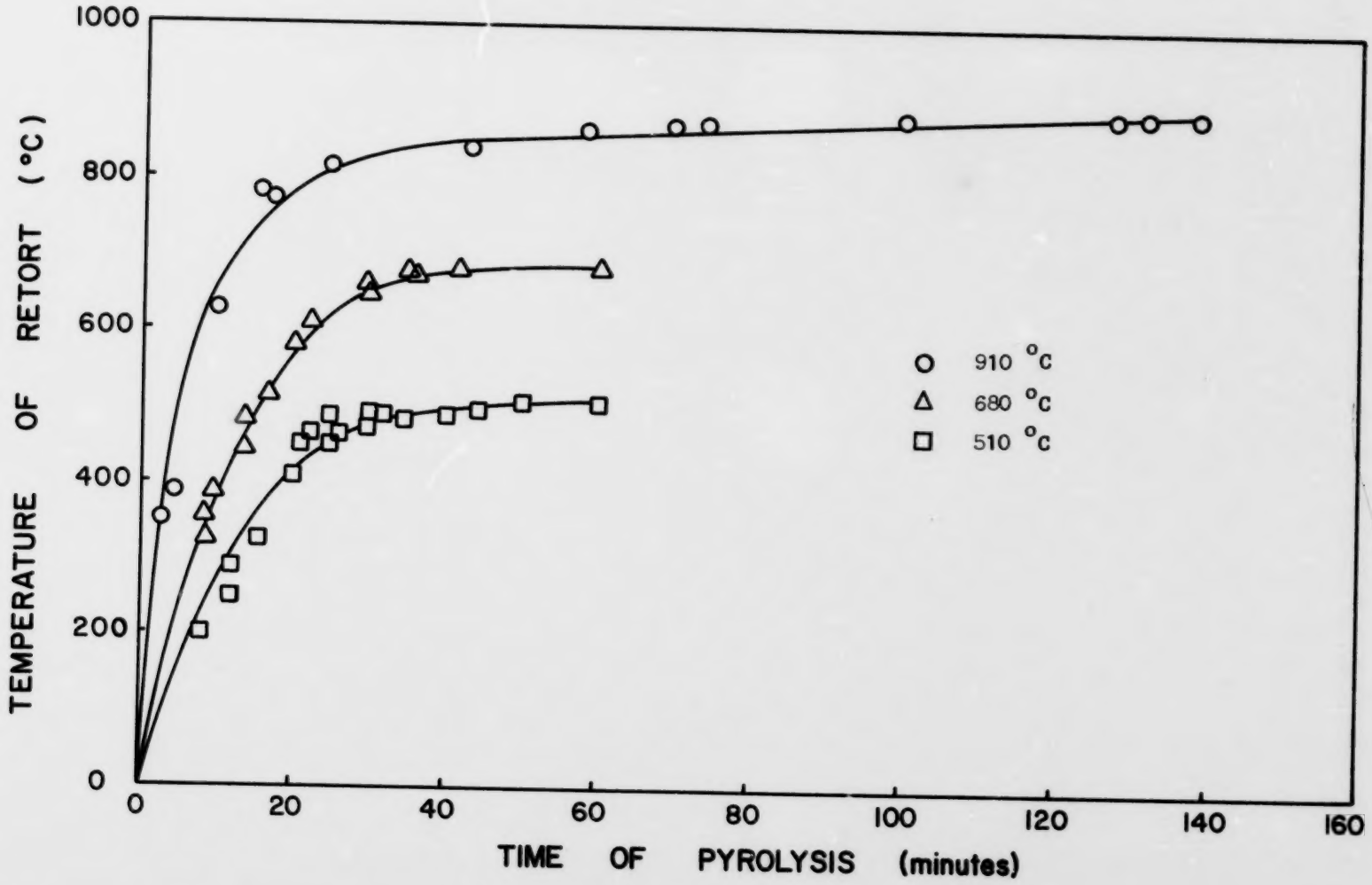

Figure 4-2. Retort temperature as a function of time for pyrolysis temperatures of 510 °C, 680 °C and 910 °C.

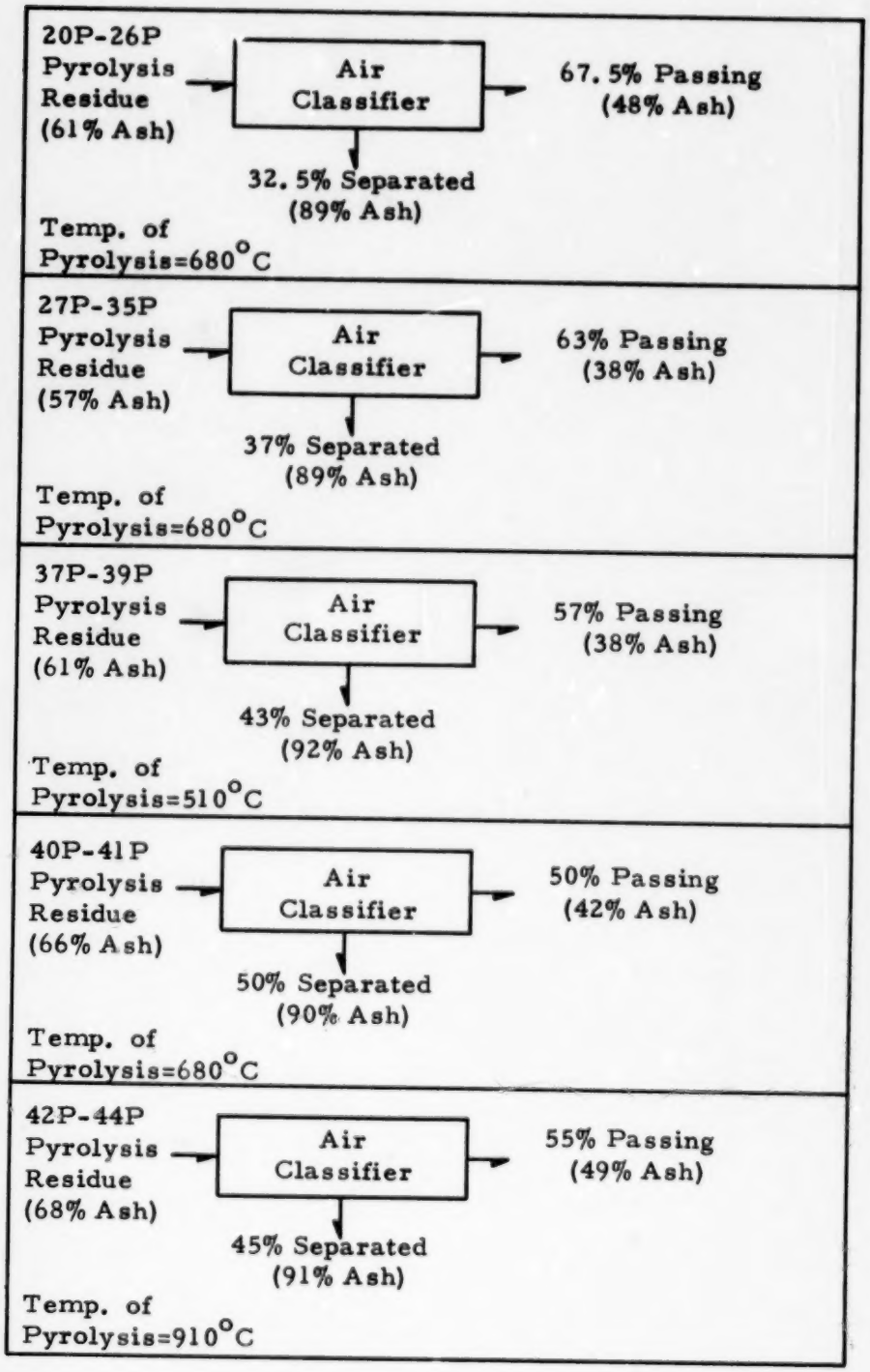

Figure 4-3. Diagram showing the effectiveness of the air classifier for ash reduction.

Classified char is much more uniform than unclassified char, and the activated carbons prepared from the classified char have a significantly lower ash content as would be expected.

IV. ACTIVATION STUDIES

A. Activation Atmosphere Studies

Activation of refuse chars (air classified) was accomplished with N_2 saturated with water vapor (N_2 sat. H_2O), a steam-N_2 mixture (steam), carbon dioxide (CO_2), a steam-carbon dioxide mixture (steam + CO_2), and an air-CO_2 mixture (air). Results of steam, CO_2, steam + CO_2 and air activations are shown in Table 4-3.

Characterization of the adsorptive capacities of activated materials is required in order to evaluate the effectiveness of the various activation schemes. Air classified refuse chars activated to about 35 percent gross weight loss with steam, CO_2, and steam + CO_2 atmospheres have COD adsorptive capacities about the same as Aqua Nuchar A (Table 4-4).

Evaluation of carbons activated with N_2 sat. H_2O and air was limited. Carbons activated with steam and with N_2 sat. H_2O have similar adsorptive properties because the activating gas (H_2O) is the same; steam activation, however, is achieved much more rapidly. Refuse carbons, activated at 910 C to percent gross weight losses of 35 percent, require 90 minutes of activation time for N_2 sat. H_2O and only 20 minutes of activation time for steam. Because steam is so much more effective, the activation and evaluation of carbons prepared with N_2 sat. H_2O is of little practical interest. Air activated carbons were erratic in composition because portions of the char would, in some cases totally oxidize to ash. The results of air activation

TABLE 4-3

THE AVERAGE PERCENT GROSS WEIGHT LOSSES ACHIEVED FOR DIFFERENT ACTIVATION ATMOSPHERES (40.0 g char samples were used).

Activated Carbon	Activation Atmosphere	Activation Temperature (°C)	Time of Activation (minutes)	Percent Gross Weight Loss (%)	Percent Ash (%)
Steam	Steam 6.5g/min. N_2 2ℓ/min.	910 °C	20 min.	35.0%	51.5%
CO_2	CO_2 9 g/min.	910	45	34.7	52.8
Steam + CO_2	Steam 4 g/min. CO_2 5.4 g/min.	910	20	35.4	51.7
Air*	Air 2ℓ/min. CO_2 6 g/min.	350	70	23.4	50.2

* Air activated carbons were not prepared from the same char sample as Steam, CO_2 and Steam + CO_2.

TABLE 4-4

CHARACTERIZATION PARAMETERS FOR REFUSE ACTIVATED CARBONS PREPARED WITH DIFFERENT ACTIVATION ATMOSPHERES.

Carbon	Methylene Blue Number	Iodine Number	Phenol Number	COD Correlation Factor*	Surface Area (M^2gm)
Aqua Nuchar A	151	560	28	1.00	625 M^2/gm
Steam	122	585	20	0.95	396
CO_2	102	535	23	0.99	413
Steam - CO_2	108	605	22	0.95	405
Air	-	-	-	$\simeq$ 2.0	-

* See Chapter 3 for definition of COD correlation factor.

experiments (Appendix A) indicate that activation temperatures as low as 350 C can be used. Adsorption properties of air activated carbons were not compared to other refuse activated carbons because the desired percent gross weight losses needed for a valid comparison were not obtained (Table 4-3).

The steam activation atmosphere was selected for further study because of the short activation time required to produce a good COD adsorbent. Although the steam + CO_2 atmosphere is as effective as steam, the assumption is made that steam alone may be more economical and easier to maintain.

Each of the refuse activated carbons in Table 4-3 is a composite of three or four carbons prepared from the same refuse sample and activated under similar conditions.

B. Percent Weight Loss Studies: Experimental Results and Interpretation

1. Relationship Between Percent Weight Loss and Activity.

The amount of carbon and volatile matter removed from a char during activation can be used as a measure of the activity of carbons produced from that char. Since refuse carbons have ash contents that are both high and variable, a distinction will be made between two types of weight losses which occur.

The percent weight loss (burn-off) is defined as the percent, by weight, of the elemental carbon portion of the char lost during activation. The term 'activation yield' is also used to describe the weight losses which occur; activation yield is equal to 100 percent minus the percent weight loss [6].

The <u>percent gross weight loss</u> is defined as the percent reduction in weight of the bulk char sample during activation. The bulk char is composed

of ash, volatile matter and elemental carbon. The activated carbon is composed of ash and elemental carbon*.

The percent weight losses and the percent gross weight losses for activated carbons 83-A to 88-A and steam are given in Table 4-5.

The effect of percent gross weight loss on phenol, iodine, methylene blue and COD adsorptive capacity is shown in Figure 4-4. Experimental values of MB No., P No., I No., COD c.f. and surface area for carbons 83-A to 88-A and steam are given in Table 4-6.

The char used for the percent weight loss studies was pyrolyzed at a temperature of 680 C. Similar char samples were used in the preparation of carbons 83-A to 88-A and steam. The percent volatile matter in the char is 16.2 percent (Table 4-5).

The percent weight loss is used as a measure of the degree of activity of an activated carbon [4,6], and, for a given primary carbon, the activity is a reproducible function of the percent weight loss [7]. The percent gross weight loss is also related to activity [7, 35].

Kipling [7] states that for percent weight loss studies, the primary carbon should be heated to the activation temperature in an inert atmosphere, prior to activation, to remove volatile char constituents. For the current study, char sample 84-A was heated to the activation temperature (910 C) and stripped with N_2 for 20 minutes. The percent volatile matter was determined to be 16.2 percent, and this value was considered standard for all chars used to prepare the carbons listed in Table 4-5.

The percent weight losses are calculated by dividing the percent carbon lost during activation (percent gross weight loss - 16.2 percent

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*Hereafter referred to simply as carbon.

[volatiles]) by the percent carbon in the primary carbon (100 percent - percent ash in the primary carbon - 16.2 percent), or

$$\text{Percent weight loss} = \frac{\text{\% gross weight loss - 16.2\%}}{\text{\% carbon in primary carbon}} \times 100\%$$

The percent ash in the primary carbon is calculated from the percent ash in the activated carbon prepared from that particular primary carbon. The total amount of ash is found to be constant, within experimental error, before and after activation.

Activated carbon 83-A had an unusually high ash content (Figure 4-5) and data for this carbon are not used for percent weight loss activity relationships.

The apparent decrease in carbon activity at percent gross weight losses greater than 45 percent (Figure 4-4) is accounted for by the high ash content of the refuse carbons. As the percent weight loss increases, the percent ash increases (Figure 4-5) leaving less carbon per unit weight of activated material. The presence of ash apparently does not affect the adsorptive capacity of the carbon portion of the activated material, but ash does contribute to the gross weight of the material and causes a reduction in the adsorptive capacity (on a bulk weight basis).

The net effect of the percent weight loss on activity can be determined by expressing the characterization parameters on the basis of a unit weight of carbon (carbon only) and plotting the calculated parameters as a function of percent weight loss. The characterization parameters, on a unit weight of carbon basis, are determined by dividing the actual (bulk) characterization parameter by the percent of carbon (100 percent - percent ash) in the

TABLE 4-5

COMPOSITION OF PRIMARY CARBONS USED TO PREPARE REFUSE ACTIVATED CARBONS 83-A TO 88-A AND STEAM, AND THE PERCENT GROSS WEIGHT LOSSES AND PERCENT WEIGHT LOSSES WHICH OCCURRED ON ACTIVATION. TEMPERATURE OF ACTIVATION WAS 910 °C.

Activated Carbon	Activation Atmosphere and Time (minutes)	Percent Ash in Activated Carbon	Percent Gross Weight Loss	Percent Ash in Primary Carbon (Calculated)	Percent Volatile Matter in Primary Carbon	Percent Elemental Carbon in Primary Carbon	Percent Weight Loss (Carbon only)
84-A	N_2 - 20 min.	42.3%	16.2%	35.4%	16.2%	48.4%	0%
83-A	Steam - 5	54.8	25.5	40.8		43.0	21.7
85-A	Steam - 10	45.0	29.4	31.8		52.0	25.4
Steam	Steam - 20	51.5	35.0	33.5	Assumed to be 16.2% for all carbons.	50.3	37.3
88-A	Steam - 30	61.0	42.0	35.4		48.4	53.2
86-A	Steam - 40	66.5	45.4	36.3		47.5	61.5
87-A	Steam - 60	85.0	55.0	38.3		45.5	85.3

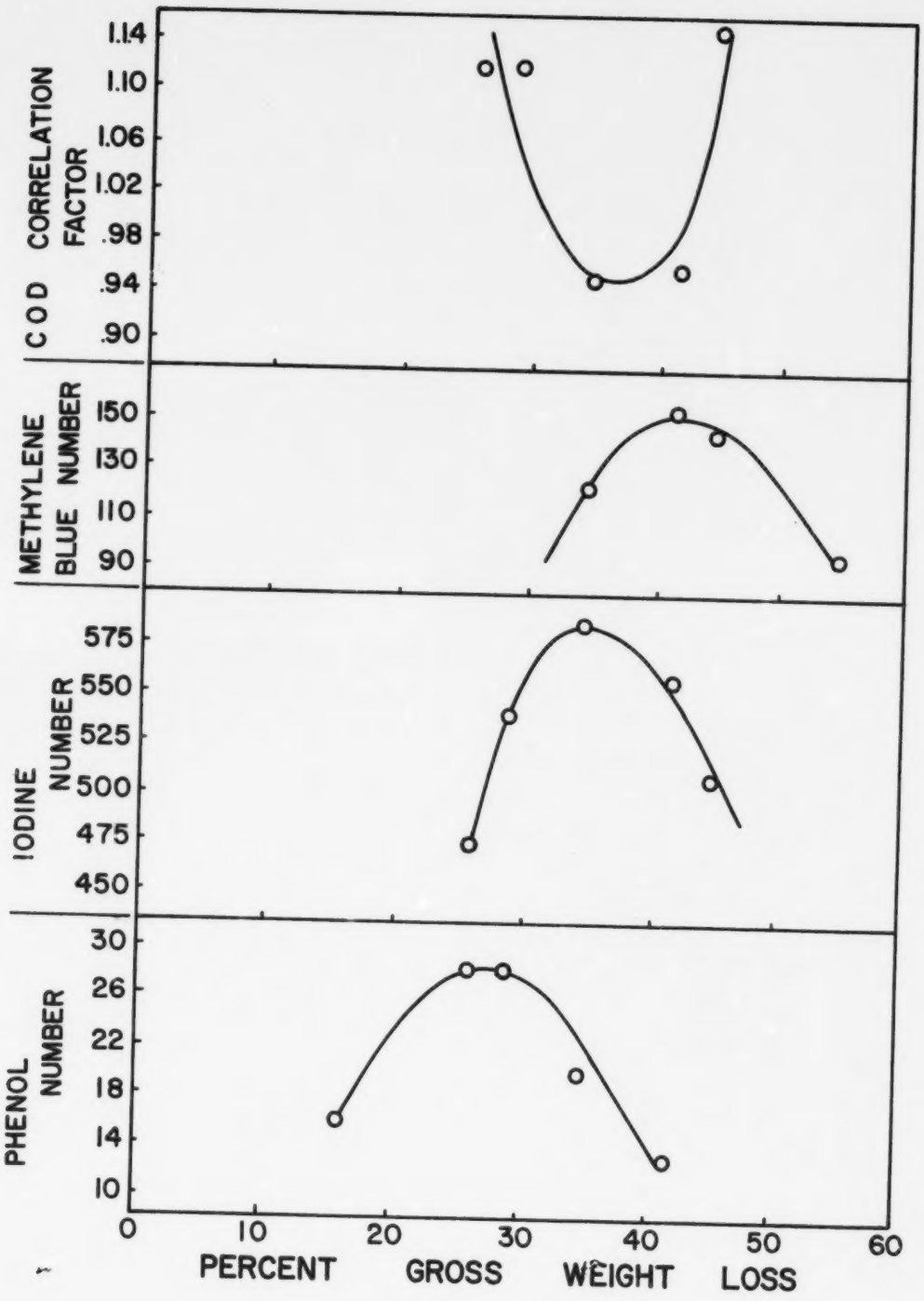

Figure 4-4. The relationship of COD, methylene blue, iodine and phenol adsorptive capacities to percent gross weight loss.

TABLE 4-6

CALCULATED CHARACTERIZATION PARAMETERS ON A UNIT WEIGHT OF CARBON BASIS

Activated Carbon	Percent Elemental Carbon in Activated Carbon	Methylene Blue Number		Phenol Number		Iodine Number		COD Correlation Factor		Surface Area (M^2/gm)	
		Actual*	Unit Wt. of Carbon	Actual*	Unit wt. of Carbon	Actual*	Unit Wt. of Carbon	Actual*	Unit Wt. of Carbon	Actual*	Unit Wt. of Carbon
84-A	57.7	-	-	16	27.8	-	-	-	-	-	-
83-A	45.2	<60	-	28	62.0	475	1050	1.12	0.523	-	-
85-A	55.0	<60	-	28	50.0	540	980	1.12	0.635	392	713
Steam	48.5	122	252	20	41.3	585	1210	0.95	0.475	396	816
88-A	39.0	153	392	13	30.0	560	1435	0.96	0.386	418	1072
86-A	33.5	145	433	10	29.9	510	1525	1.15	0.397	413	1232
87-A	14.8	95	642	3	-	375	-	-	-	-	-

* Actual values are determined by experiment.

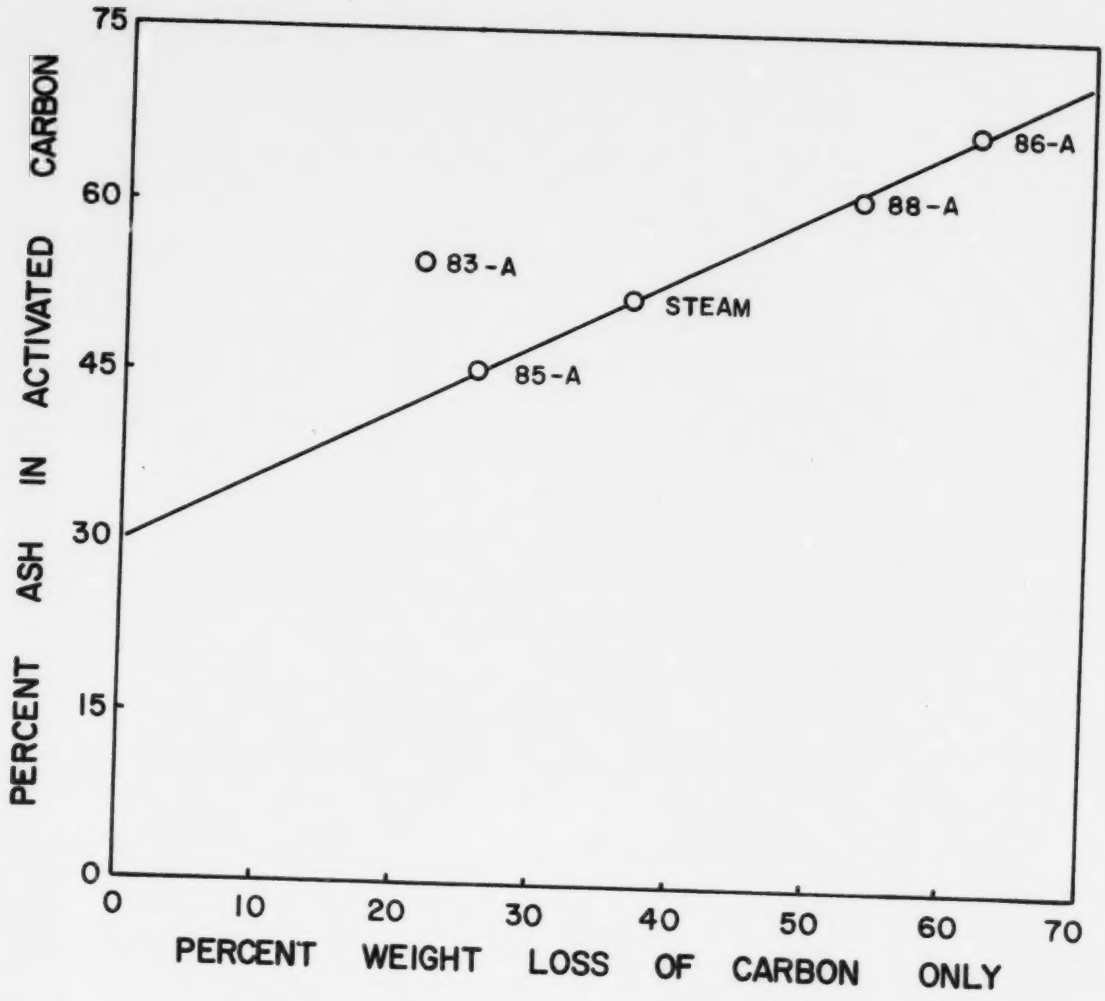

Figure 4-5. Relationship between percent ash and percent weight loss for carbons 83-A, 85-A, 86-A, 88-A and steam.

activated carbon (Table 4-6). Characterization parameters, on a unit weight of carbon basis, are plotted as a function of percent weight loss in Figures 4-6 and 4-7. A straight-line relationship has been assumed for simplicity. The surface area and adsorptive capacities for methylene blue, iodine and COD are shown to increase with increasing percent weight loss. Adsorptive capacity for phenol decreases with increasing percent weight loss. There is, however, an optimum percent weight loss for maximum phenol adsorption between 0 percent and 25 percent.

The optimal percent weight loss required to maximize the adsorptive capacity for a particular adsorbate can be calculated. By determining the relationship of both the ash content and activity (for the particular adsorbate) to the percent weight loss for the carbon used, the optimal percent weight loss can be determined. For the case of methylene blue and refuse activated carbon, the relationship of methylene blue activity and percent weight loss can be determined graphically from a plot similar to Figure 4-6; the linear relationship is

$$\text{MB No./unit wt. C} = -30 + 8\ (\text{percent weight loss})$$

The relationship between percent ash and percent weight loss is also linear (Figure 4-5); the relationship is Percent Ash = 30 + 0.59 (percent weight loss). By appropriate algebraic manipulations (see Appendix B) the methylene blue number is found as a function of the percent weight loss only:

$$\text{MB No.} = [-30 + 8.0\ (\text{percent weight loss})]\left[1 - \frac{(30 + 0.59\ [\text{percent weight loss}])}{100}\right]$$

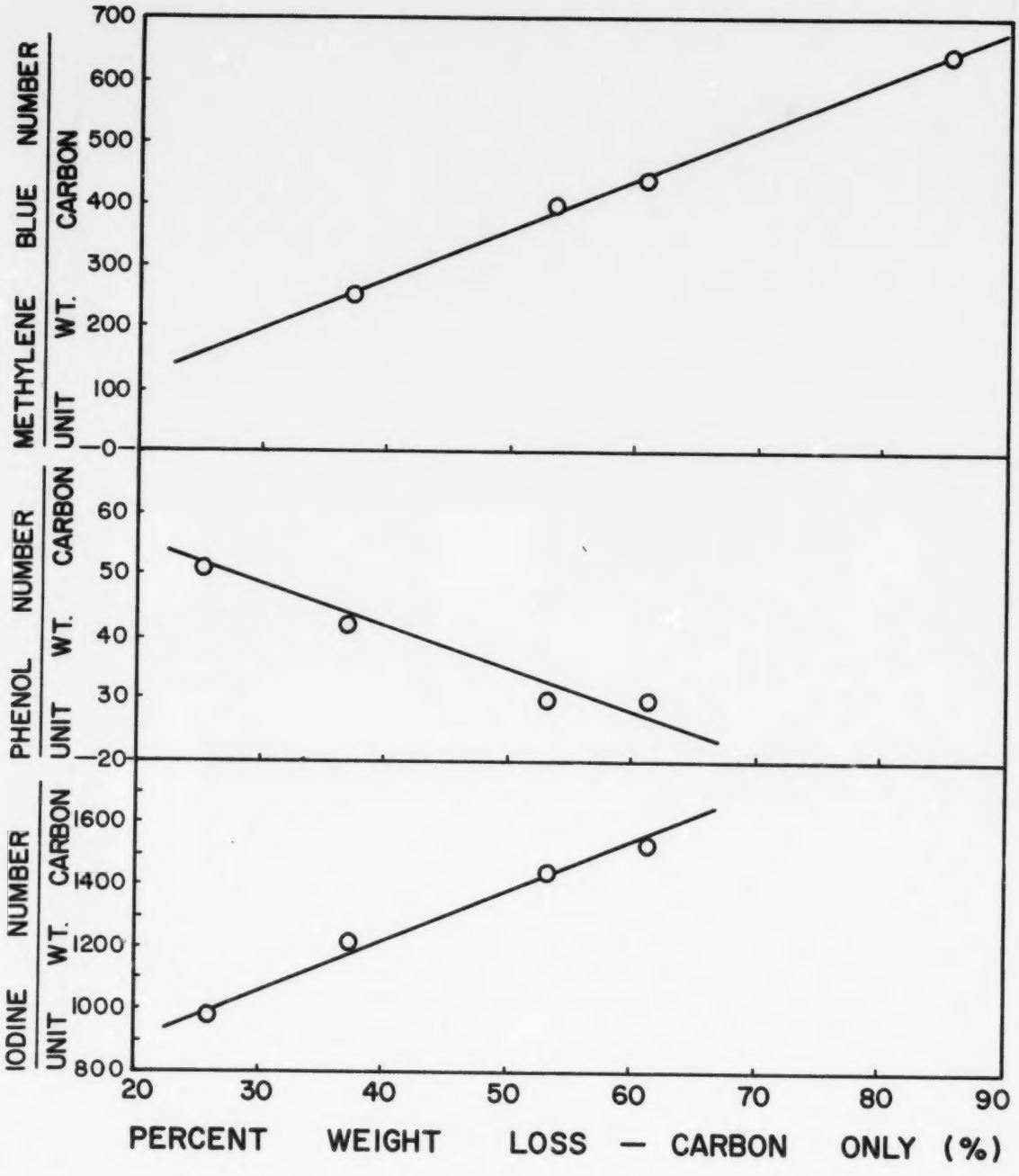

Figure 4-6. Relationship of iodine, phenol, and methylene blue numbers, on a unit weight carbon basis, to percent weight loss.

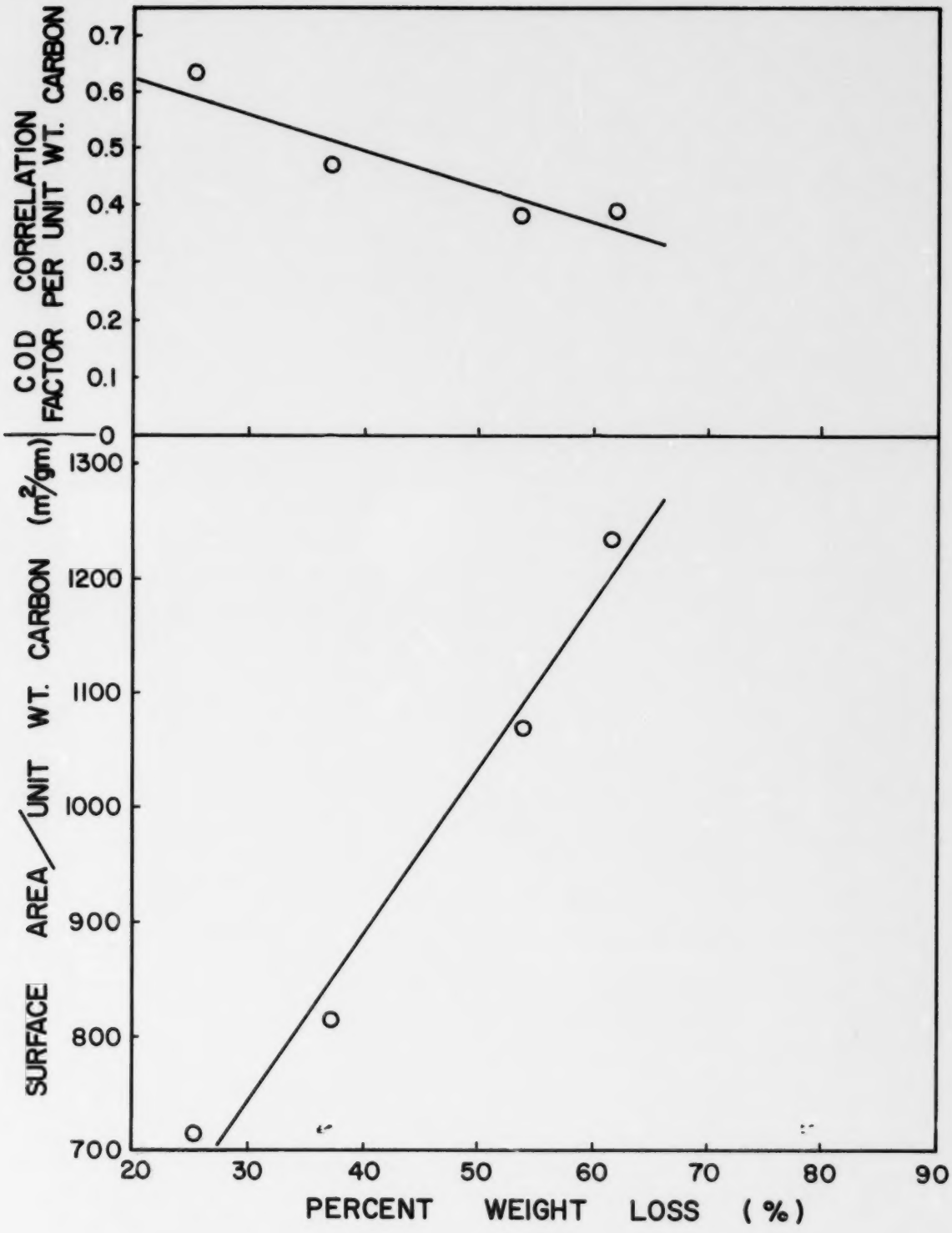

Figure 4-7. The relationship of COD c. f. and surface area, on a unit weight carbon basis, to percent weight loss.

Setting d (MB No.)/d (percent weight loss) = 0, and solving for percent weight loss, the calculated value is 59.2 percent. Calculations are in Appendix B. Using the same method, the optimum percent weight loss for iodine and COD adsorption is found to be 38.4 percent and 49.6 percent, respectively (Appendix B). The calculated percent weight losses are in agreement with experimental results (Table 4-7).

2. Effect of Activation Temperature on the Rate of Percent Gross Weight Loss with a Steam Activation Atmosphere.

Similar primary carbons were activated at temperatures of 800 C and 910 C. Steam was supplied at a constant rate of ca. 6.5 g/min. to 40.0g samples of char. The rate of percent gross weight loss at 800 C is about 0.25 percent/min., while the rate at 910 C is 0.50 percent/min. A plot of percent gross weight loss as a function of time for activation temperatures of 800 C and 910 C is shown in Figure 4-8.

The rate of percent gross weight loss is determined by taking the slope of the percent gross weight loss versus time plots (Figure 4-8). Percent gross weight loss cannot be predicted from the rate data alone because of the different values of percent gross weight losses at 0 minutes activation time. The difference in the percent gross weight losses at 0 minutes is attributed to the additional pyrolysis which occurs at the higher activation temperature (910 C). The variation in initial percent gross weight loss does not allow the direct use of rate data for design purposes.

For the 680 C char used in this study, the percent gross weight loss required for maximum COD adsorptive capacity is about 35% (Figure 4-4). At 800 C, the time required to obtain a 35% gross weight loss is approximately 100 minutes. Under similar conditions, the time required at 910 C is about

TABLE 4-7

CALCULATED PERCENT WEIGHT LOSSES FOR MAXIMUM ADSORPTION OF METHYLENE BLUE, IODINE AND COD

Activated Carbon	Percent Weight Loss (%)	Methylene Blue Number	Calculated Percent Weight Loss for Maximum MB Number (%)	Iodine Number	Calculated Percent Weight Loss for Maximum I Number (%)	COD Correlation Factor	Calculated Percent Weight Loss for Maximum COD c.f. (%)
85-A	25.4%	< 60		540		1.12	
Steam	37.3	122		585		0.95	
88-A	53.2	153	59.2%	560	38.4%	0.96	49.6%
86-A	61.5	145		510		1.15	

20 minutes (Figure 4-8). Activation with steam at 800 C appears impractical because of the higher costs associated with a larger furnace and increased steam requirements.

3. Effect of Activation Temperature on the Efficiency of Oxidation of Carbon and Volatiles with Steam.

The weight of carbon and volatile matter which is oxidized, or otherwise lost, during activation is plotted as a function of the weight of steam supplied at temperatures of 800 C and 910 C in Figures 4-9 and 4-10, respectively. With excess steam provided, 1 g of steam at 800 C oxidizes 0.0109 gm of carbon and volatile matter; at 910 C, the ratio is 0.029 gm/gm steam.

The amount of carbon and volatile matter oxidized per unit weight of steam is found by taking the slope of the curves in Figures 4-9 and 4-10.

From the stoichiometry of the basic steam-carbon oxidation reaction suggested by Smisek and Cerny [6],

$$C + H_2O \rightarrow CO + H_2$$

1.5 g of steam will oxidize 1 g of carbon. Since a considerable amount of excess steam was supplied to the carbon (much more than the stoichiometric requirement) the rate at which the carbon oxidizes is limited by the steam-carbon reaction rate. At 910 C the reation rate is about three times greater than the rate at 800 C; the conclusion is that activation with steam is much more efficient at 910 C than at 800 C.

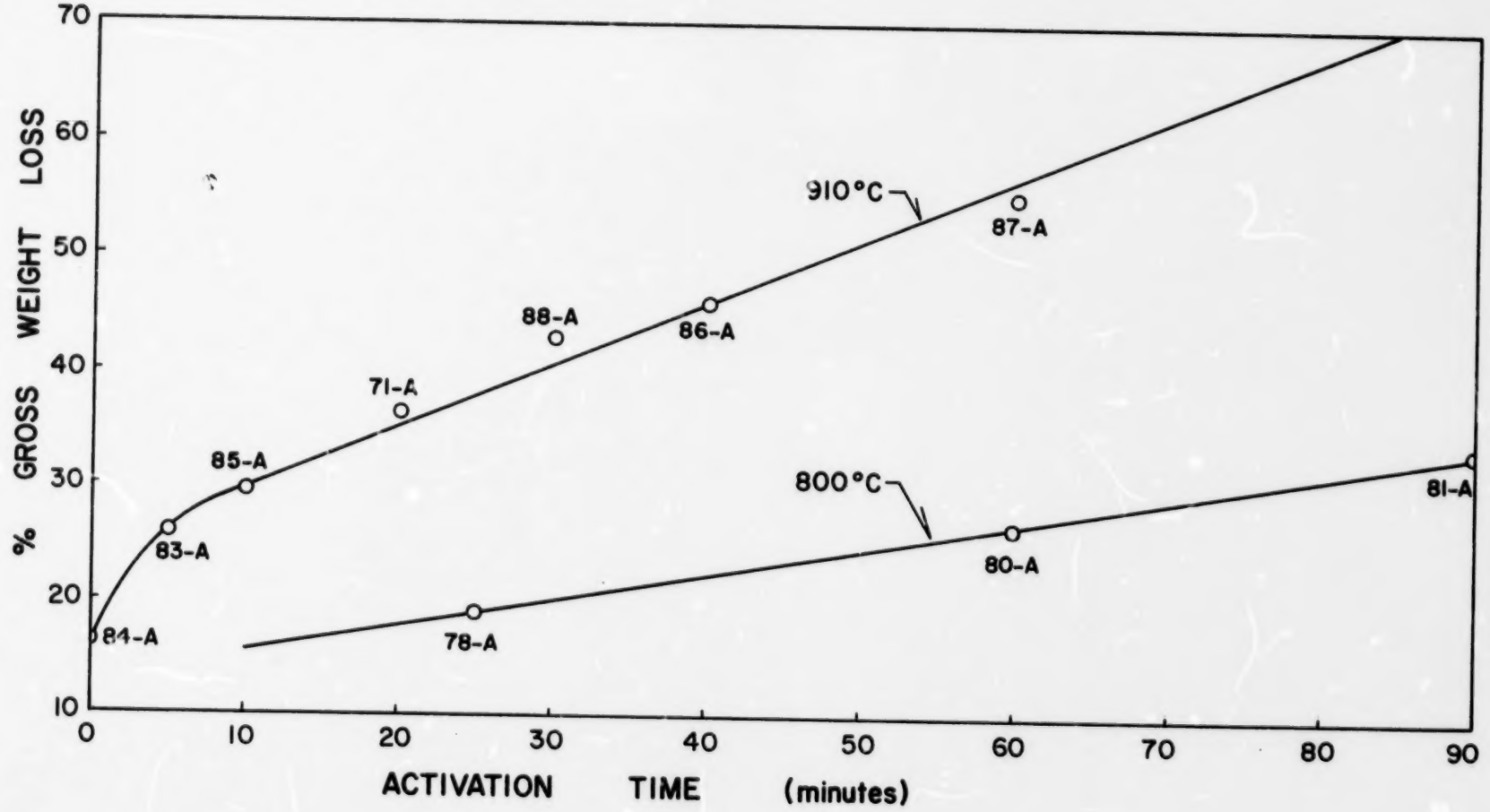

Figure 4-8. Effect of time on percent gross weight loss for a steam activation atmosphere at temperatures of 800 °C and 910 °C.

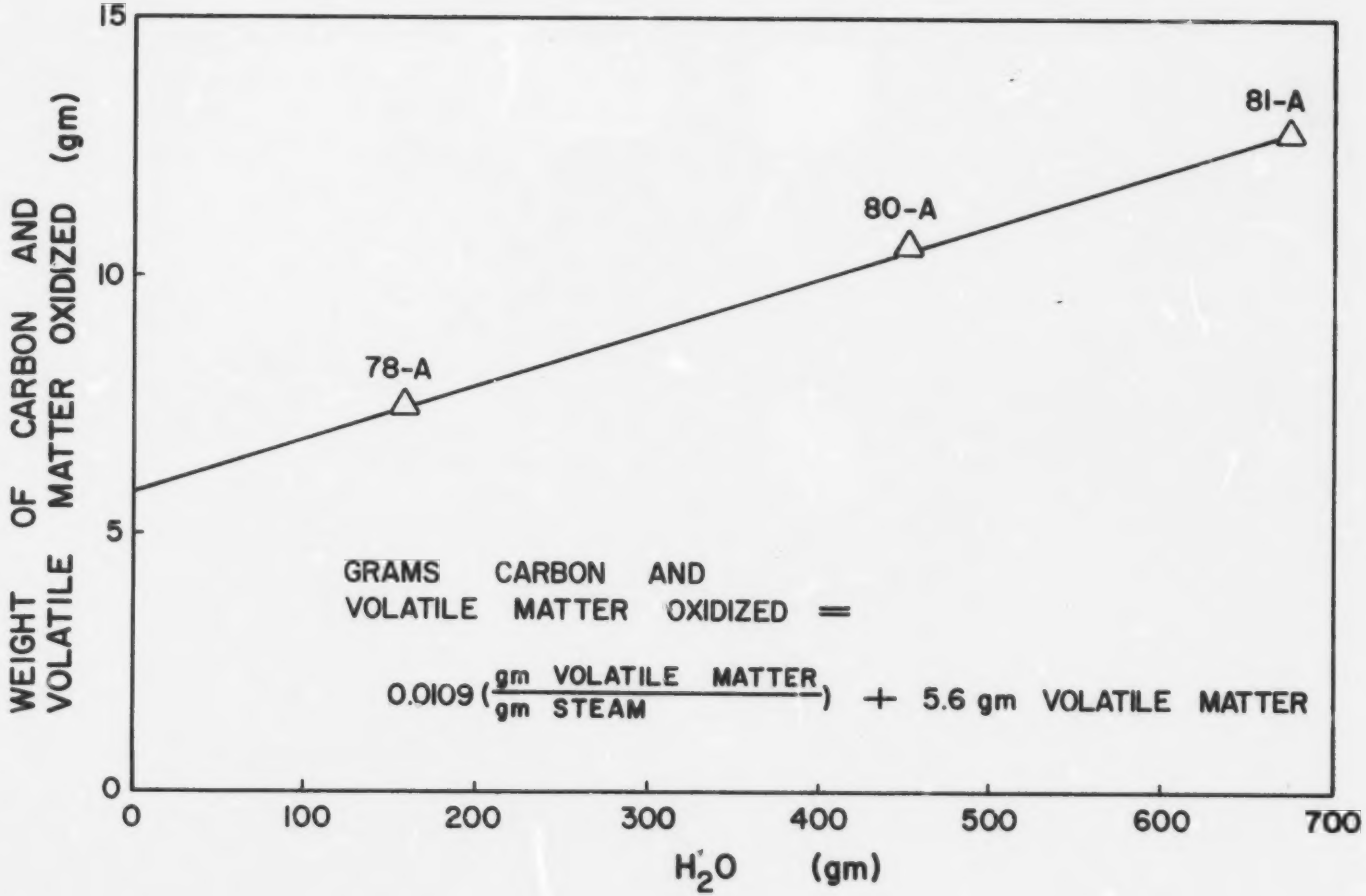

Figure 4-9. Weight of carbon and volatile matter oxidized as a function of the quantity of steam at 800 °C.

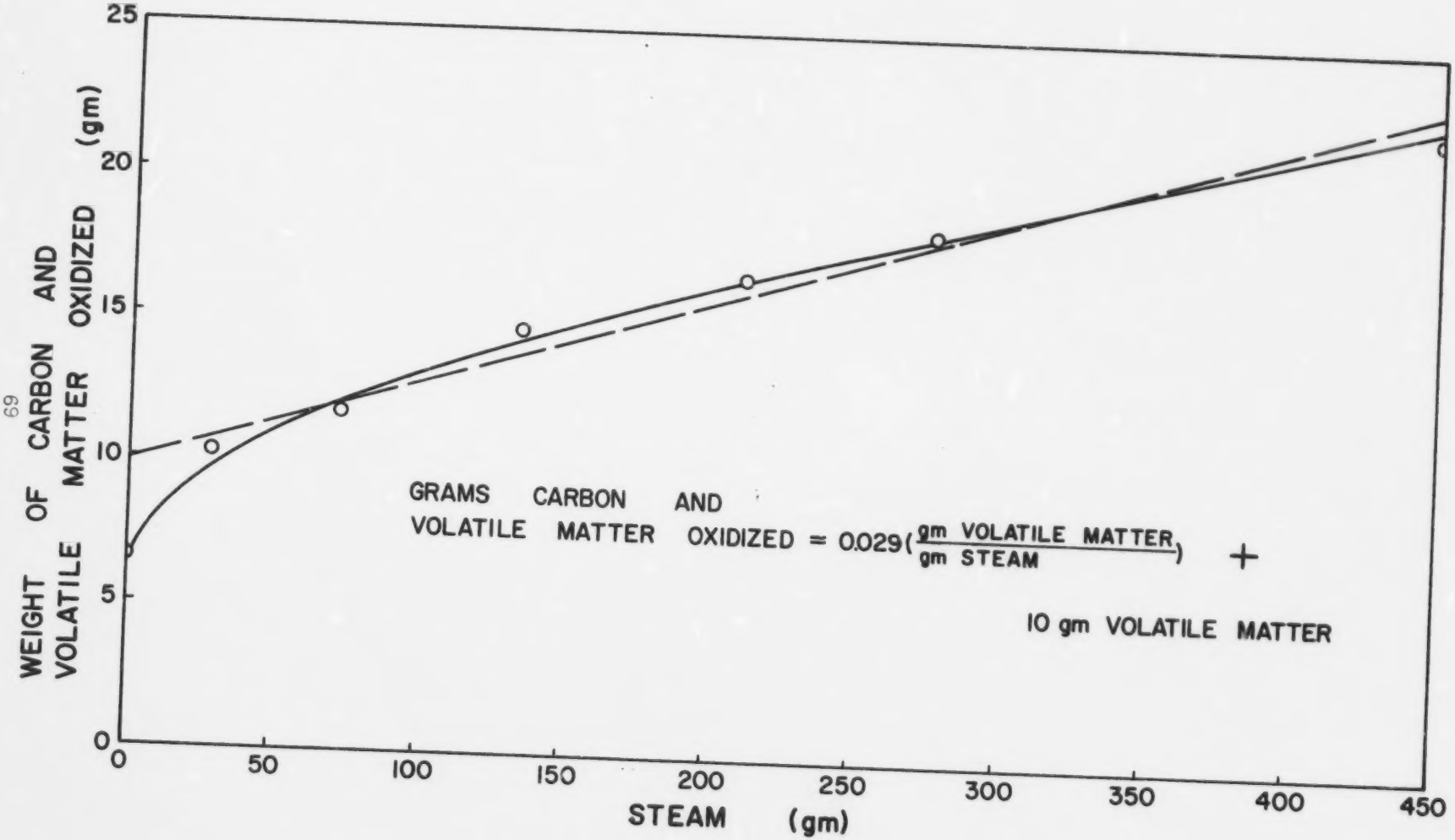

Figure 4-10. Weight of carbon and volatile matter oxidized as a function of the quantity of steam at 910 °C.

TABLE 4-8

CHARACTERIZATION PARAMETERS FOR ACTIVATED CARBONS PREPARED FROM CHARS PRODUCED AT DIFFERENT PYROLYSIS TEMPERATURES AND ACTIVATED AT 910 °C.

Activated Carbon	Pyrolysis Temperature of Primary Carbon	Activation Atmosphere and Time (minutes)	Percent Gross Weight Loss (%)	Percent Ash in Activated Carbon (%)	Methylene Blue Number	Iodine Number	Phenol Number	COD Correlation Factor
93-A	510	Steam* - 20	44.8%	61%	139	495	15	1.07
95-A	680	Steam - 20	41.3	58	121	490	22	0.98
99-A	910	Steam - 20	34.8	64	142	465	15	0.86
94-A	510	Steam - 30	48.8	71	128	415	9	0.90
97-A	680	Steam - 30	46.2	75	98	<325	6	0.96
101-A	910	Steam - 30	46.7	70	118	375	5	0.82
96-A	510	CO_2** - 45	48.0	70	130	365	10	0.88
98.A	680	CO_2 - 45	47.5	65	138	425	18	0.80
100-A	910	CO_2 - 45	41.3	68	137	370	12	0.86

* Steam at 6.5 g/min.

** CO_2 at 9 g/min.

C. Activation Studies of Primary Carbons Produced at Different Pyrolysis Temperatures.

The effect of pyrolysis temperatures on adsorptive properties of activated carbons has been studied. Activated carbons were prepared from refuse samples pyrolyzed at 510 C, 680 C and 910 C. The resultant chars were activated with both steam and CO_2 at 910 C.

The adsorptive properties of the activated carbons prepared from chars produced at the different pyrolysis temperatures are approximately the same (Table 4-8). No significant differences have been noted.

Carbons 93-A, 95-A and 99-A were steam activated at 910 C for 20 minutes (Table 4-8). The methylene blue and phenol numbers for these carbons, shown in Table 4-8, indicates a discrepancy for 95-A. On closer look, however, the lower than expected ash content of 95-A implies that a char sample with a higher than average carbon content was used to prepare that carbon. If this is the case, the percent gross weight loss is lower than expected, and an explanation for the high phenol number and low methylene blue number exists. Examination of Figure 4-4 shows that methylene blue numbers are low and phenol numbers are high for the lower percent gross weight losses. A similar method of examination of other carbons in Table 4-8 shows that no significant difference in adsorptive capacities exists.

The values of the characterization parameters for carbons 93-A to 101-A are within the range of values for other refuse carbons having similar percent gross weight losses and ash contents (Tables 4-4, 4-6).

D. The Effect of Selected Catalysts on the Activation of Refuse Carbons.

Carbons which were impregnated with selected catalysts (e.g., $NaCO_3$, KOH, etc.), prior to activation, did not exhibit any noticeable increase in adsorptive capacity when compared to non-catalyzed carbons having similar percent gross weight losses and ash contents.

The results of activation studies involving catalysts are given in Tables 4-9 and 4-10. Catalysts do increase the rate at which carbons are oxidized during activation. The average percent gross weight losses for the catalyzed carbons in Table 4-9 is about 27 percent, while the average loss for the uncatalyzed carbons (11-A, 23-A to 25-A, 28-A) is about 20 percent.

The bulk of the work done with catalysts was performed on chars which were not air classified prior to activation. Unclassified chars are high in ash and have a large variability in composition. Activation of these chars can produce good adsorbents, but the comparison of adsorptive properties of chars of this nature is difficult because of variable ash contents and inconsistent percent gross weight losses. A general comparison of catalyzed chars with non-catalyzed chars, on a unit weight of carbon basis, indicates that no significant increase in adsorptive capacity can be attributed to catalysts.

The initial work on activation was performed with a fixed bed reactor. In such a bed, contact of the activating gases with the char is restricted (compared to a fluid bed). Catalyzed chars activated in the fixed bed are better adsorbents than the non-catalyzed chars activated under similar conditions. The increased adsorptive capacity results from the fact that

TABLE 4-9

PERCENT GROSS WEIGHT LOSSES AND SOME ADSORPTIVE PROPERTIES OF REFUSE ACTIVATED CARBONS PREPARED WITH CATALYSTS.

Activated Carbon	Time of Contact with N_2 saturated with H_2O at 910 °C.	Catalyst, Percent by Weight, Used	Percent Gross Weight Loss	Percent Ash	Methylene Blue Number	Iodine Number	Comments
11-A	148 min.	none	21.3%	-	-	-	None of the carbons were air classified prior to activation.
23-A	90	none	28.3	58%	105	-	
24-A	90	none	19.5	-	101	-	
25-A	90	none	14.0	-	< 65	-	
28-A	90	none	18.8	55	< 65	-	
12-A	90	5% Na_2CO_3	35.8	-	-	447	
13-A	90	5% Na_2CO_3	35.5	-	>140	520	
14-A	120	5% Na_2CO_3	29.5	65	107	468	
15-A	90	3% Na_2CO_3	28.1	-	-	417	
27-A	90	3% Na_2CO_3	19.8	-	-	-	
16-A	90	1% Na_2CO_3	30.6	-	<80	471	
22-A	90	1% Na_2CO_3	23.2	61	120	-	
17-A	90	5% $CaCO_3$	26.9	62	-	481	
18-A	90	5% NaCl	26.5	-	97	483	
19-A	90	5% KOH	22.9	65	90	520	
20-A	90	3% CuO	24.0	-	-	485	
21-A	90	5% $ZnCl_2$	25.3	-	98	-	

TABLE 4-10

PERCENT GROSS WEIGHT LOSSES AND SOME ADSORPTIVE PROPERTIES OF REFUSE ACTIVATED CARBON PREPARED WITH Na_2CO_3 AS A CATALYST. TEMPERATURE OF ACTIVATION WAS 910 °C

Activated Carbon	Activation Atmosphere and Time in Minutes	Catalyst, Percent by Weight, Used	Percent Gross Weight Loss	Percent Ash	Methylene Blue Number	Iodine Number	Comments
31-A	CO_2 - 90	none	33.8	75%	105	-	
32-A	CO_2 - 90	none	32.5	77	105	250	
33-A	CO_2 - 90	2% Na_2CO_3	41.5	91	< 78	-	
34-A	CO_2 - 45	none	24.0	66	≃105	-	
35-A	CO_2 - 45	2% Na_2CO_3	27.0	74	≃105	420	
42-A	Steam - 15	2% Na_2CO_3	31.1	-	115	450	
44-A	Steam - 15	none	22.8	-	115	400	
45-A	Steam + CO_2 20	none	20.2	75	90	333	
46-A	Steam + CO_2 20	2% Na_2CO_3	27.5	72	105	260	
47-A	Steam + CO_2 25	none	20.2	66	90	360	
48-A	Steam + CO_2 25	2% Na_2CO_3	30.0	78	114	260	
89-A	Steam - 20	none	33.8	53	121	613	Carbons 89-A to 92-A Air Classified prior to activation. 89 and 90 are more efficient for COD removal than 91 and 92 (Appendix C-7).
90-A	Steam - 20	none	34.3				
91-A	Steam - 20	2% Na_2CO_3	34.3	57	144	600	
92-A	Steam - 20	2% Na_2CO_3	36.6				

burn-off proceeds more effectively for the catalyzed chars (carbon oxidation is very sensitive to catalysts [44, others]). When a fluid bed is used, however, burn-off proceeds effectively for both catalyzed and non-catalyzed chars. In this study, no significant effect of catalysts on the activation process was noted when the fluid bed reactor was used.

The catalytic properties of Na_2CO_3 has been investigated most extensively because of the common use of carbonates of alkali metals in commercial activation processes [6]. The addition of Na_2CO_3 to char did result in an increase in percent gross weight losses during activation (Tables 4-9, 4-10), but not in a consistent manner (probably due to the nature of the char). Adsorptive capacity does not appear to be significantly improved by use of Na_2CO_3 (Table 4-10).

Carbons 91-A and 92-A were carefully prepared from air classified char impregnated with 2 percent Na_2CO_3. Carbons 89-A and 90-A were prepared in a similar manner, but without catalysts. Evaluation of the COD adsorptive capacity, as well as the other parameters given in Table 4-10, shows that the catalyzed carbon has an adsorptive capacity similar to the non-catalyzed carbon.

When it was determined that the fluid bed could be used to produce good adsorbents without catalysts, the project emphasis was shifted to other areas. Studies on chemical catalysts were not pursued further for the following reasons: First, the use of catalysts for the activation of refuse carbon does not appear to have any beneficial effects on adsorptive properties. Second, the use of catalysts would increase the dissolved solids leaching from the carbon (unless processed prior to use). Third, additional process

and chemical costs arising from catalyst contact systems, chemical feed systems and chemical storage would result. Finally, the burn-off needed to produce good adsorption characteristics for refuse carbons can be obtained in a fluid bed without the use of catalysts.

V. CARBON CHARACTERIZATION AND EVALUATION

A. Comparison of Refuse Activated Carbons with Three Commercial Activated Carbons.

A comparative approach has been used to evaluate the adsorption characteristics of activated refuse carbons. Several readily available commercial activated carbons are used for comparative purposes. Characterization parameters for Aqua Nuchar A, Calgon BL, Darco M and a typical refuse activated carbon are given in Table 4-11. Most comparative work in this investigation utilizes Aqua Nuchar A on the standard powdered activated carbon. Aqua Nuchar A was chosen because it is a good quality, low cost powdered activated carbon which has been studied extensively for use in waste water treatment processes [58, 59, 60] and is commonly used for practical applications. Refuse activated carbons compare favorably with the commercial carbons for COD adsorption.

A typical refuse carbon is considered to have been activated at 910 C to a 40 percent gross weight loss with steam or CO_2 and contains from 55 percent to 65 percent inert material. The values of the characterization parameters for the refuse carbon given in Table 4-11 were selected from Tables 4-4, 4-6, 4-8. The ranges of the values given are typical for refuse activated carbons produced during this study.

The carbon fraction of the refuse activated carbon is very active.

TABLE 4-11

CHARACTERIZATION PARAMETERS FOR THREE COMMERCIAL ACTIVATED CARBONS AND A TYPICAL REFUSE ACTIVATED CARBON.

Activated Carbon	Percent Ash (%)	Methylene Blue Number	Iodine Number	Phenol Number	COD Correlation Factor	Surface Area (M^2/gm)	Apparent Density
Aqua Nuchar A	3.5%	151	560	28	1.00	625 M^2/gm	0.26
Calgon BL	8	278	920	33	0.95*	1113	-
Darco M	16.5	125	455	21	0.97**	627	-
Refuse Carbon***	55-65	100-145	425-600	10-20	0.9-1.1	350-400	0.40

* Correlation factor based on one COD isotherm only (3/10/71). Appendix 3-A.

** Correlation factor based on one COD isotherm and one TOC isotherm (9/1/71. Appendices 3-G, 3-H.

*** Air classified before and after pyrolysis; steam activated at T $\simeq$ 910 ^{o}C to a 35 percent to 45 percent gross weight loss.

The high activity of the carbon fraction is evident when the characterization parameters for commercial and refuse carbons are compared on a unit weight of carbon basis, as in Table 4-12. Inert material, which makes up over half of the weight of the refuse activated carbon, does not contribute significantly to adsorptive capacity.

The COD adsorptive capacity is considered to be the most important carbon characterization parameter from a practical view point. The results of numerous COD adsorption tests are summarized in Table 4-13. Graphical display of COD adsorption experimental results are shown in Appendices C-3 to C-13. Based on the results obtained, refuse activated carbons are as effective as Aqua Nuchar A for COD removal.

B. Pore Size Distribution of Refuse Activated Carbons

The pore size distribution of Aqua Nuchar A and several refuse activated carbons are shown in Figure 4-11. For Aqua Nuchar A, 70 percent or more of the total pore volume is composed of pores less than 20 angstroms in radius. On the other hand, the refuse activated carbons only have 10 percent, or less, of the total pore volume composed of pores having radii of less than 20 angstroms.

The lack of micropores in refuse carbons which, according to Smisek and Cerny [6], usually contributed 95 percent of the carbon surface areas, agrees with the generally low surface areas of refuse carbons. The high adsorptive capacity of the refuse carbons can be partially attributed to the increased accessibility to the inner micropores which is offered by the high percentage of large (macro- and transitional) pores. The transitional and macropore structure has the advantage of being less susceptible to blockage by macromolecules and colloidal matter. When using adsorbents in heterogenerous solutions like sewage, high transitional and macropore volumes are an advantage.

TABLE 4-12

CHARACTERIZATION PARAMETERS FOR THREE COMMERCIAL ACTIVATED CARBONS AND A TYPICAL REFUSE ACTIVATED CARBON ON A UNIT WEIGHT OF CARBON BASIS.

Activated Carbon	Percent Carbon in Activated Carbon (%)	Methylene Blue Number Per Unit Weight of Carbon	Iodine Number Per Unit Weight of Carbon	Phenol Number Per Unit Weight of Carbon	Surface Area Per Unit Weight of Carbon (M^2/gm)
Aqua Nuchar A	96.5%	157	580	29	650 M^2/gm
Calgon BL	92	302	1000	36	1210
Darco M	83.5	150	545	25	750
Refuse Carbon	35-45	250-360	1050-1500	25-50	875-1000

TABLE 4-13

COD CORRELATION FACTORS FOR REFUSE ACTIVATED CARBONS ACTIVATED UNDER DIFFERENT CONDITIONS.

Activated Carbon	COD Correlation Factor					
	6/26/71 * Palo Alto Primary	6/28/71 Palo Alto Primary	7/1/71 San Jose Secondary	8/23/71 Palo Alto Primary	9/1/71 Palo Alto Primary	Average
Aqua Nuchar A	1.00	1.00	1.00	1.00	1.00	1.00
Steam	0.98	0.77	0.96	0.94	1.09	0.95
CO_2	1.00	0.85	0.97	1.15	0.96	0.99
Steam + CO_2	0.94	0.82	1.00	1.00	-	0.95
Air	2.00	-	-	-	-	2.0

* Denotes Sewage Sample Used.

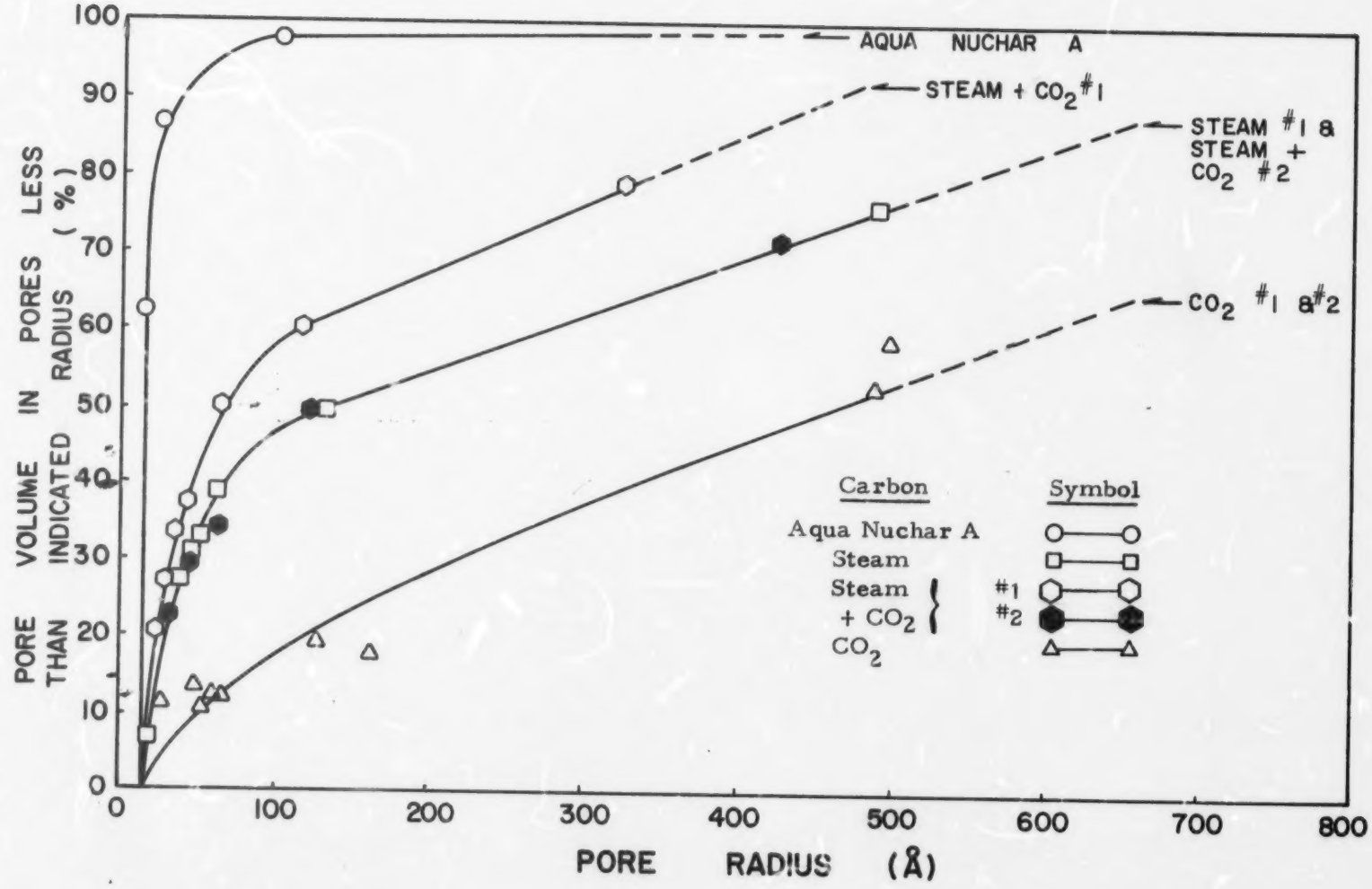

Figure 4-11. Pore volume distribution for Aqua Nuchar A and some typical refuse activated carbons.

C. Characterization of Leachates from Refuse Activated Carbons

Leachates from refuse activated carbon were compared with the leachates from Aqua Nuchar A and Darco M. The experimental results are given in Table 4-14. The refuse carbon leachates are more alkaline, have more hardness and have more dissolved solids than the leachates from Aqua Nuchar A and Darco M.

The variability of the dissolved solids values in Table 4-14 can be attributed to experimental error. The data can be used, however, to obtain an estimate of the order of magnitude of the dissolved solids in the leachates.

D. Scanning Electron Photomicrographs of Aqua Nuchar A and Refuse Activated Carbon

Use has been made of scanning electron photomicrographs as an additional means of comparative analysis of refuse activated carbons. Information on particle size distribution and particle morphology is readily obtained from scanning electron photomicropgraphs. At present electron microscopy can only be accepted as an auxiliary method for the analysis of carbons; it can however, provide useful information when properly applied.

Scanning electron photomicrographs of Aqua Nuchar A (ANA) and refuse activated carbon are shown in Figures 4-12 and 4-13, respectively.

Comparison of Figures 4-12A and 4-13A shows that ANA has a much more uniform morphology and a smaller average particle size than the refuse carbon. Almost all of the ANA particles (Figure 4-12A) have a maximum dimension of less than 25 μm, while a majority of refuse carbon particles (Figure 4-13A) have a maximum dimension of more than 25 μm. Refuse activated carbons have an extremely broad range of particle sizes. Electron photomicrographs for CO_2 activated carbons indicated similar particle size distributions and the same general particle morphology.

TABLE 4-14

LEACHATES FROM COMMERCIAL AND REFUSE ACTIVATED CARBONS

Activated Carbon	Carbon Dose (mg/1)	pH	Specific Conductance (Micromhos/cm)	Alkalinity as $CaCO_3$ (mg/1)	Hardness as $CaCO_3$ (mg/1)	Sodium (mg/1)	Dissolved Solids (mg/1)
Aqua Nuchar A	400	6.50	18.0	5	3	0.74×10^{-2}	45.4
	801	6.70	33.5	5	7	3.4×10^{-2}	54.5
	1200	6.80	39.1	5	10	5.0×10^{-2}	56.0
Darco M	401	6.40	12.7	2.5	3	0.23×10^{-2}	35.0
	801	6.45	27.4	3.0	9	1.6×10^{-2}	-
	1201	6.60	29.0	3.5	8	2.5×10^{-2}	30.0
88-A*	400	7.65	24.7	12	10	-	40.5
	801	9.18	33.5	17	17	-	55.5
	1200	9.70	44.0	19	24	$<.23 \times 10^{-2}$	58.0

* Carbon 88-A - Steam activated at 910 °C from 30 minutes to a gross weight of 42 percent; ash content is 61 percent.

A

B

C

Figure 4-12

Scanning electron photomicrographs of Aqua Nuchar A

Magnification and Scale:

A - 200x
1 cm = 50 μm

B - 2000x
1 cm = 5 μm

C - 10000x
1 cm = 1 μm

A

B

C

Figure 4-13

Scanning electron photomicrographs of refuse activated carbon. The carbon shown is steam activated at 910°C and has 61% ash.

Magnification and Scale:

A - 200x
1 cm = 50 μm

B - 2000x
1 cm = 5 μm

C - 10000x
1 cm = 1 μm

The shape of the individual carbon particles is clearly shown in Figures 4-12B and 4-13B. The refuse activated carbon appears to be flaky (Figure 4-13A) while ANA, shown in Figure 4-12B, is more compact and clump-like.

The fineness of the structure of the carbon particles is shown in Figures 4-12C and 4-13C. ANA is much finer than the refuse carbon, and the carbon sheets appear to be packed closely together (Figure 4-12C). The refuse carbon seems to be composed of larger carbon sheets that are more widely spaced; the successive layers of the carbon sheets are clearly shown in the photomicrograph (Figure 4-13C). The large percentage of macro and transitional pore volume of the refuse carbons may be due to the large carbon sheets. The large and relatively widespaced sheets also justify the assumption that the interior micropores of the carbon are more accessible to adsorbates (Section V-B of this chapter).

VI. PRIMARY CARBON EVALUATION

A. Effectiveness of Primary Carbon for COD Removal

Refuse was pyrolyzed at 680 C and the resulting char and Aqua Nuchar A were compared for the effectiveness of COD removal. The experimental results are summarized in Table 4-15. Primary carbon is found to be very inferior to activated carbon (Aqua Nuchar A) for COD removal. Primary char has only one-fifteenth the adsorptive capacity of Aqua Nuchar A. Comparative COD adsorption isotherms for primary carbon and activated carbon are shown in Appendices D-2 to D-5.

The experimental data indicate dosages of primary char required to effectively remove COD from waste waters would be enormous (on the order

TABLE 4-15

COD CORRELATION FACTORS FOR PRIMARY (UNACTIVATED) CARBON

Carbon	COD Correlation Factor +				
	2/27/71 * Palo Alto Primary	3/2/71 Palo Alto Primary	3/3/71 San Jose Secondary	4/12/71 Palo Alto Primary	Average
Aqua Nuchar A	1.0	1.0	1.0	1.0	1.0
Primary	18.6	15.9	17.2	9.5	15.3

* Denotes sewage samples used.

\+ Refer to Appendix D for addtional data.

of several thousand mg/1). The use of massive dosage of primary carbon for removal of organics would create such problems as storage, application, sludge disposal and, possibly, dissolved solids leaching from the char.

B. Effectiveness of Primary Carbon for Methylene Blue and Iodine Adsorption

Primary carbon is a poor adsorbent for methylene blue and iodine. The M.B. No. and I No. of primary carbons have values less than 31 and 150, respectively. Aqua Nuchar A has corresponding values of about 150 and 560 for M.B. No. and I No., respectively. The difference is striking. Due to the large carbon sample sizes required to determine the exact M.B. No. and I No., the tests are considered impractical.

VII. EVALUATION OF REFUSE ACTIVATED CARBON FOR WASTE WATER TREATMENT PROCESS DESIGN

Refuse activated carbon was compared to Aqua Nuchar A for use as an adsorbent in the physical-chemical treatment of sewage. Aqua Nuchar A is a good quality, low cost powdered activated carbon which has been studied extensively for use in waste water treatment processes [58, 59, 60] and is commonly used for practical applications. Carbon properties which are compared include COD adsorption capacity, rate of COD adsorption and the settleability of carbon and suspended solids with the aid of alum ($Al_2[SO_4]_3 \cdot 18\ H_2O$) and ferric chloride ($FeCl_2 \cdot 6\ H_2O$). Dissolved solids, which may leach from the carbons, have been discussed in Section V-C.

A. Effectiveness for COD Removal

The correlation factor (defined in Chapter 3) has been developed for simplified comparison of COD adsorption capacity. Refuse activated carbons

usually have correla 'on factors that range from 0.9 to 1.1. Refuse carbons are as effective as Aqua Nuchar A for COD removal (Table 4-13, Appendices C-1 to C-13). Refuse carbon dosages required to achieve the same degree of COD reduction, for a given process, are approximately the same as for Aqua Nuchar A.

B. Rate of Adsorption of COD

Aqua Nuchar A was found to reduce the COD of Palo Alto primary effluent by 42 percent after 15 minutes and 45 percent after 90 minutes (Figure 4-14); an equal dose of refuse activated carbon reduced the COD of an equivalent primary effluent sample by 36 percent in 15 minutes, and 40 percent in 90 minutes (Figure 4-15). Aqua Nuchar A removed 90 percent of the total COD adsorbed in ca. 10 minutes; refuse carbon adsorbed 90 percent in ca. 15 minutes. More extensive grinding of the refuse carbon should reduce the average particle size and result in a consequent increase in the rate of COD adsorption for that carbon.

Although Aqua Nuchar A adsorbs COD more rapidly than refuse carbon, a contact time of 20 minutes would be adequate for both carbons to remove about 90 percent or more of adsorbable COD.

C. Settleability of Refuse Activated Carbon Using Alum and Ferric Chloride

The settleability of refuse activated carbon compared favorably with Aqua Nuchar A. For alum dosages of 30 mg/1 and 60 mg/1, Aqua Nuchar A settled more effectively; at an alum dose of 150 mg/1 the refuse activated carbon was superior (Figure 4-156). For $FeCl_3 \cdot 6\ H_2O$ dosages of 40 mg/1, 80 mg/1 and 120 mg/1, settling of the refuse activated carbon was more

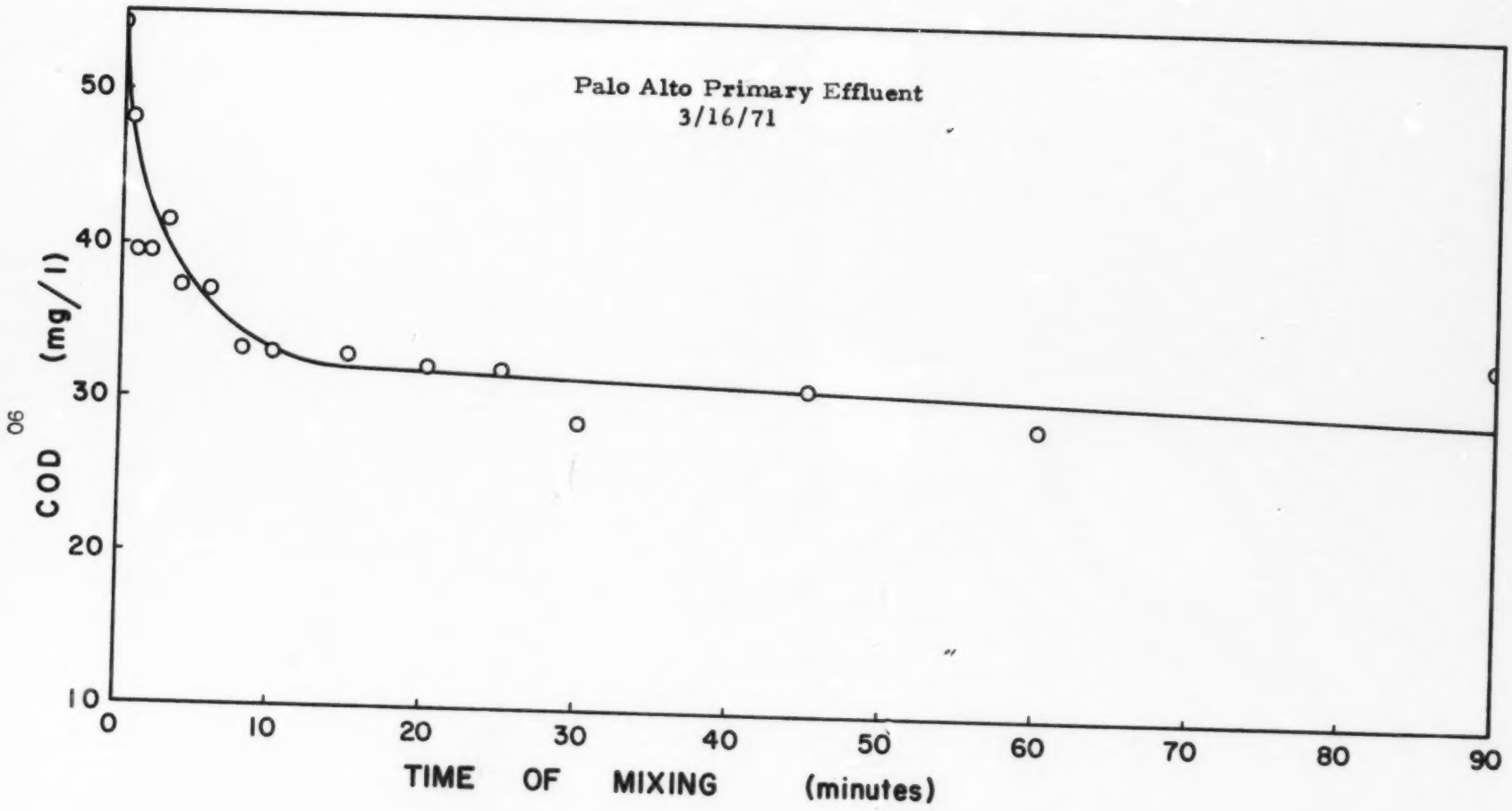

Figure 4-14. Adsorption Rate Study. COD reduction as a function of time with 1000 mg/l of Aqua Nuchar A.

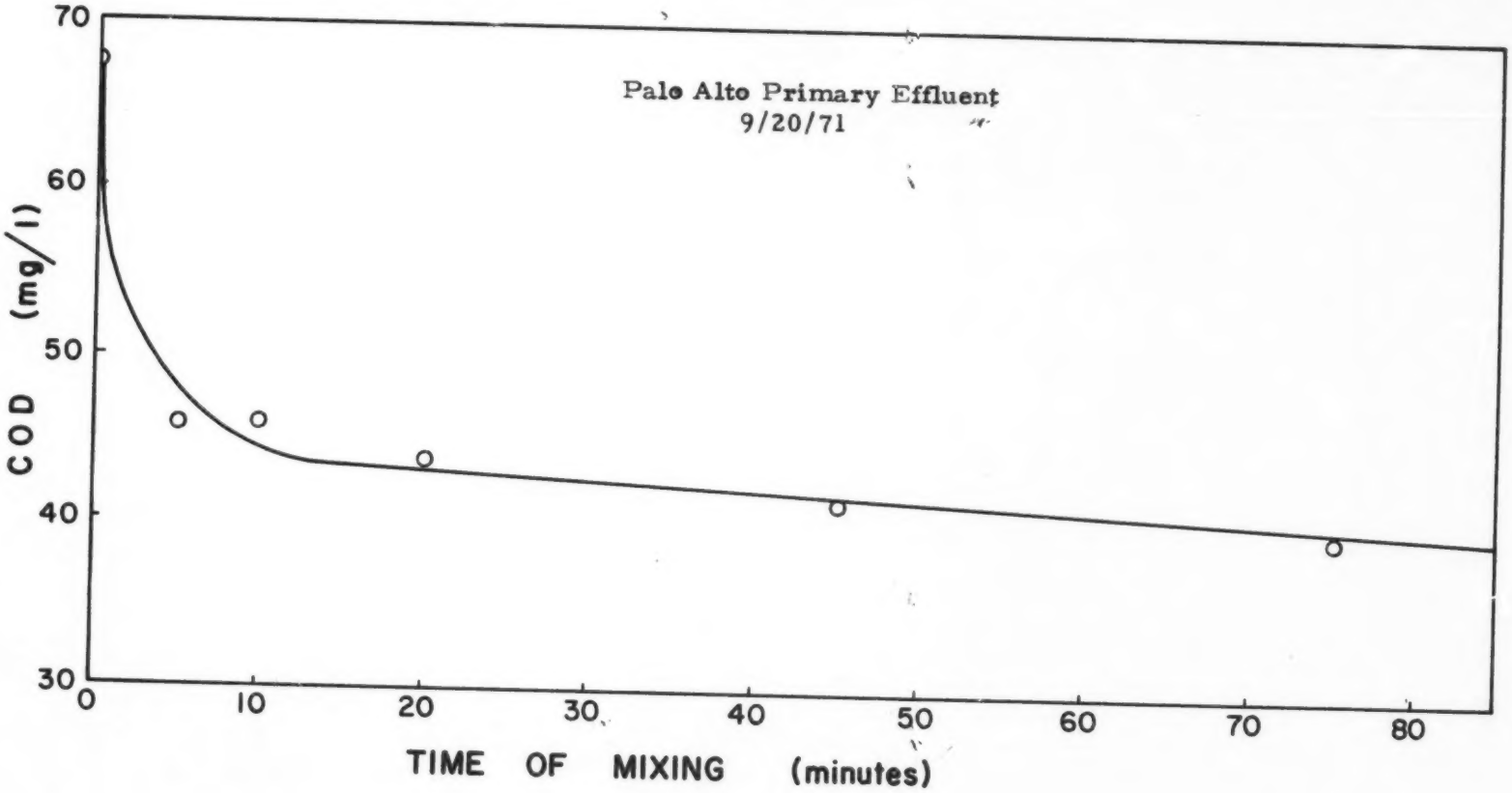

Figure 4-15. Adsorption Rate Study. COD reduction as a function of time with 1000 mg/l of refuse activated carbon (steam).

effective (Figure 4-17). Alum and $FeCl \cdot 6\ H_2O$ dosages as high as 250 mg/1 and 200 mg/1, respectively, were used; optimum doses for both carbons were 150 mg/1 of alum and 120 mg/1 of $FeCl_3 \cdot 6\ H_2O$.

VIII. YIELD OF ACTIVATED CARBON FROM REFUSE

The yields of the various processes used to produce activated carbon from raw refuse are given in Figure 4-18. When the sieving process is used, as in the preparation of carbons of a standard size for laboratory evaluation, the activated carbon yield is 8 percent; when sieving is not used, as might be the case for refuse carbons used in waste water treatment processes, the yield is 10 percent.

The yields of the processes shown in Figure 4-18 are based on a moisture content of about 30 percent for refuse, a pyrolysis temperature of 680 C and a percent gross weight loss of approximately 38 percent during activation.

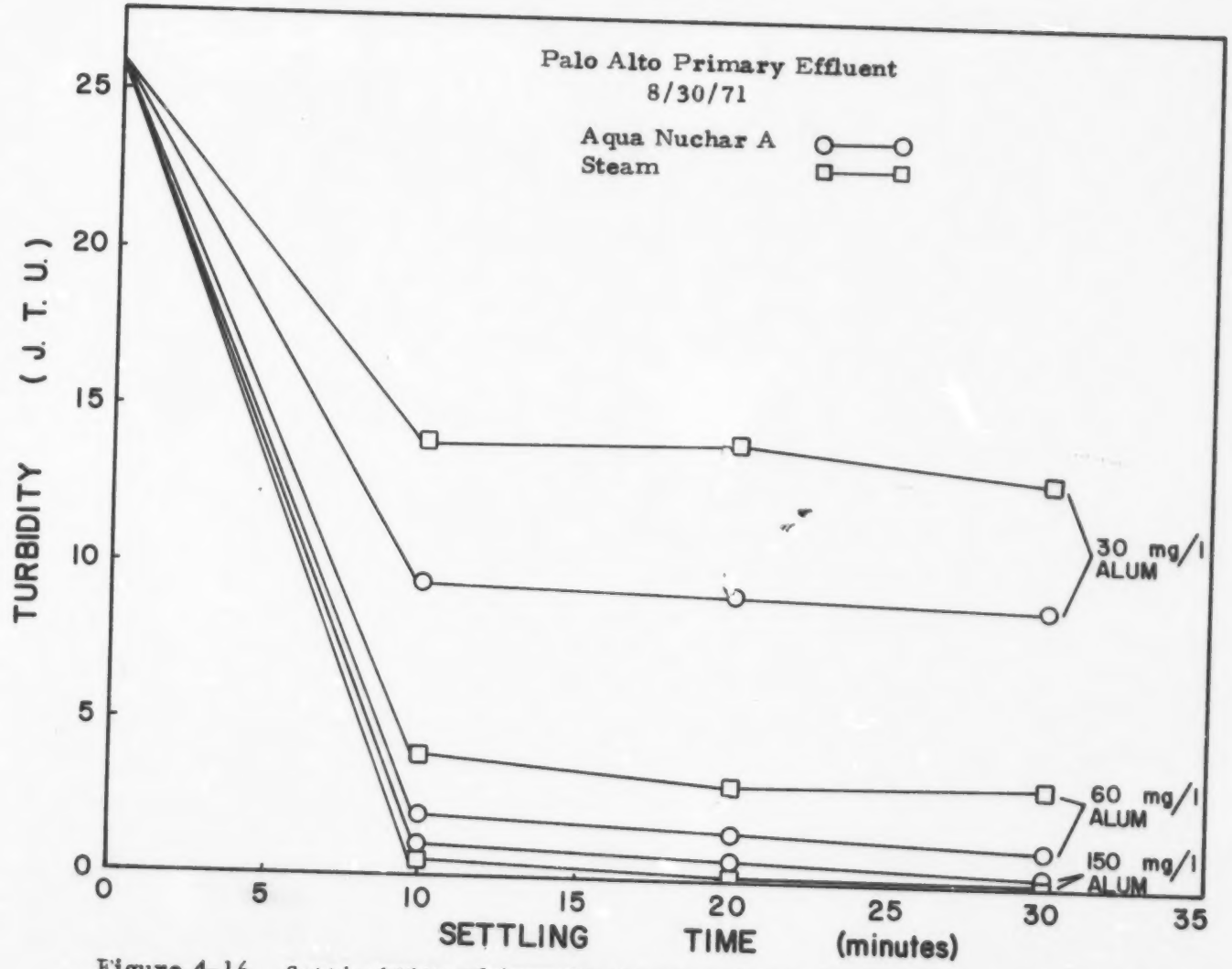

Figure 4-16. Settleability of Aqua Nuchar A and refuse activated carbon with Alum ($Al_2(SO_4)_3 \cdot 18H_2O$) dosages of 30 mg/l, 60 mg/l and 150 mg/l.

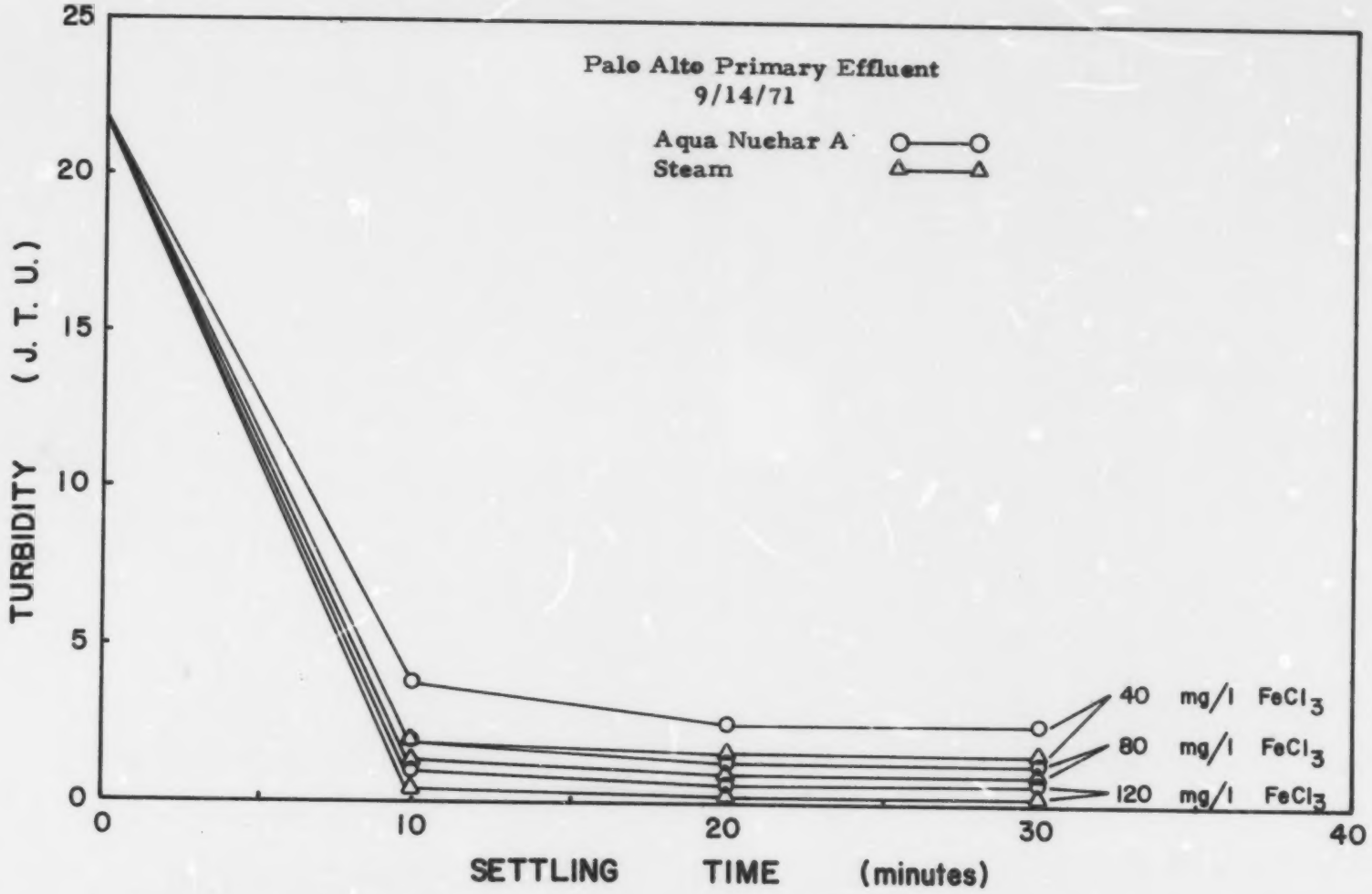

Figure 4-17. Settleability of Aqua Nuchar A and refuse activated carbon with $FeCl_3 \cdot 6H_2O$ dosages of 40 mg/l, 80 mg/l and 120 mg/l.

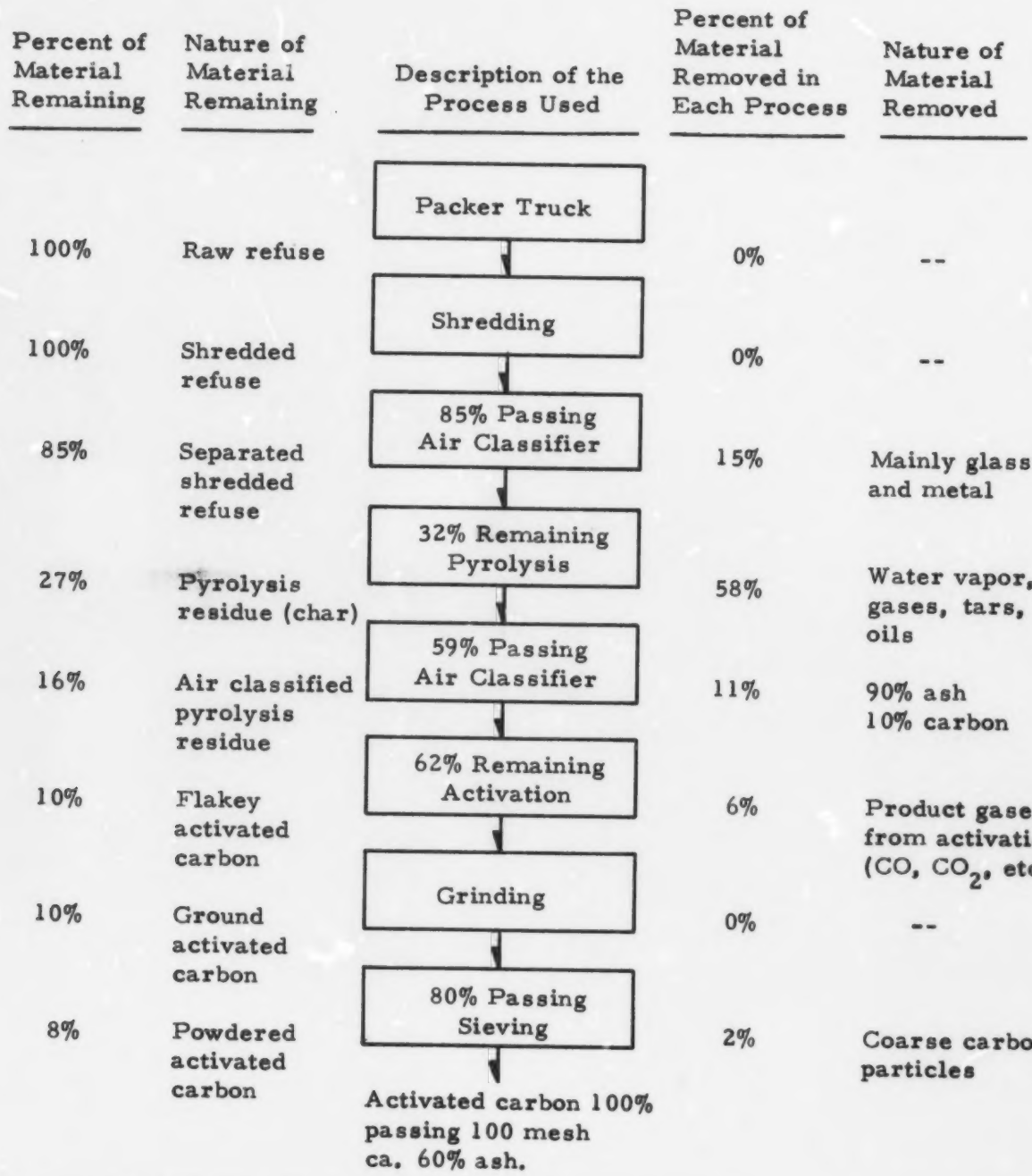

Figure 4-18. Flow diagram showing the material losses resulting from the processes used to make activated carbon from municipal refuse.

CHAPTER 5

ECONOMICAL FEASIBILITY OF WASTEWATER TREATMENT WITH REFUSE ACTIVATED CARBON

I. WASTEWATER TREATMENT WITH POWDERED ACTIVATED CARBON

Several publications on the use of powdered activated carbon for wastewater treatment suggest that the use of powdered carbon is both effective and economically competitive with other treatment processes (Table 5-1). A careful review of references [58,60,61] in Table 5-2 reveals that the cost of treatment (with powdered carbon) is very sensitive to the efficiency and cost of regeneration and the cost of make-up carbon. More efficient use of the carbon (e.g., two contact stages) reduces the carbon requirements and results in a consequent decrease in regeneration and make-up carbon costs. The economic analysis presented here has been approached from two points of view. The first approach is basically one of presenting the economics in the context of a cost per 1000 gallon treatment. The eventual estimated costs per 1000 gallons are sensitive to the estimated costs of regeneration and make-up carbon. The second approach simply discusses the costs of producing a powdered activated carbon from municipal refuse on a per pound basis. The cost of producing activated carbon from refuse is 5.5 cents/lb; if pyrolysis costs are not included, the cost is 0.93 cents/lb.

The sensitivity of the cost of treatment with powdered activated carbon to the cost of regeneration and make-up carbon is best illustrated

TABLE 5-1

COMPARISON OF LITERATURE ON TREATMENT OF WASTEWATER WITH POWDERED ACTIVATED CARBON

Investigator	Effluent to be Treated	Number of Contact Stages	Estimated Treatment Efficiency	Carbon Dose (mg/l)	Losses Expected for Carbon Regeneration	Cost for Treatment of 1000 gal. Sewage for 10 MGD Plant	Activated Carbon Used and Cost of the Carbon
Knopp, Gitchel 1970 (60)	Raw Sewage	2	90 percent COD Removal	450-500 mg/l	5 percent	13.2 cents	Aqua Nuchar A at 7 cents/lb
Shuckrow, Dawson, Olesen 1971 (58)	Raw Sewage	1	90 percent TOC Removal	600	10 percent	21.5 cents	Aqua Nuchar A at 9 cents/lb
Davies, Kaplan 1964 (59)	Secondary Effluent	1 2	85-90 percent COD Removal	750 300	5 percent	7.9 cents* 6.7 cents*	Aqua Nuchar A at 7 cents/lb
Garland, Beebe 1970 (61)	Secondary Effluent	2	80 percent COD Removal	240	10 percent	15.0 cents	Darco S-51 at 16 cents/lb

* Prices determined in 1964.

TABLE 5-2

ESTIMATED CAPITAL AND OPERATING COSTS, EXCLUSIVE OF CARBON AND REGENERATION, FOR PHYSICAL-CHEMICAL TREATMENT OF WASTEWATER WITH POWDERED ACTIVATED CARBON

Investigator	Cost of Treatment for 10 MGD Plant* (cents/10^3gal)	Estimated Percent of Cost of Treatment for Make-up Carbon and Regeneration (percent)	Estimated Capital and Operating Costs Exclusive of Carbon and Regeneration (cents/10^3gal)	Estimated Costs of Make-up Carbon and Regeneration (cents/10^3gal)	Estimated Cost of Make-up Carbon (cents/10^3gal)	Estimated Cost of Regeneration (cents/10^3gal	Estimated Cost of Regeneration Per Pound of Carbon Regenerated (cents/lb.)
Knopp, Gitchel 1970 (60)	13.2 cents	36 percent	8.4 cents	4.8 cents	1.4 cents at 7 cents/lb	3.4 cents	0.9 cents
Shuckrow, et al. 1971 (58)	21.5	58	9.1	12.4	4.5 cents at 9 cents/lb	7.9	1.75
Garland, Beebe 1970 (61)	15	45	8.2	6.8	3.2 cents at 16 cents/lb	3.6	2.00

* Cost of treatment by some investigators does not include all costs considered by others.

by an example. Estimates for the cost of regeneration of powdered carbon range from 0.9 cents to 2.3 cents/lb and Aqua Nuchar A, a typical powdered activated carbon, costs 9.5 cents/lb (F.O.B. Covington, Va.) plus 4.3 cents/lb for transportation to San Francisco. Assume that a treatment process requires 600 mg/l (5 lb/1000 gal) of powdered activated carbon and assume a low regeneration cost of 1 cent/lb with 95 percent efficiency; also assume that the activated carbon used has a cost of 8 cents/lb. Then regeneration and make-up carbon costs for such a process are 4.75 cents and 2 cents, respectively, for a total of 6.75 cents/1000 gal. If the carbon cost is increased from 8 cents/lb to 13.8 cents/lb (the cost of Aqua Nuchar A in San Francisco), the make-up carbon costs for the above process will increase from 2 cents/1000 gal to 3.45 cents/1000 gal and raise the total carbon and regeneration costs from 6.75 cents to 8.2 cents/1000 gal. If regeneration cost is increased to 2 cents /lb and is only 90 percent efficient, and Aqua Nuchar A is used, the costs of carbon and regeneration are 6.9 cents and 11 cents, respectively, for a total of 17.9 cents/1000 gal; this increases the original costs (6.75 cents/1000 gal) by almost a factor of three.

The estimated capital and operating costs for powdered carbon treatment processes, exclusive of make-up carbon and regeneration costs, are insensitive to carbon costs (Table 5-2). It is interesting to note that the capital and operating costs, exclusive of carbon and regeneration, are about the same for the treatment of raw sewage and for secondary effluent; note also that the regeneration and make-up carbon costs are not too dependent upon the type of effluent to be treated. The average capital and operating costs for the

treatment of raw sewage, exclusive of carbon and regeneration, is about 8.8 cents/1000 gal [58,60].

In a recent article by Hopkins, et al. [62], the cost of primary treatment was estimated to be 11.6 cents/1000 gal for a 10 MGD plant. A similar type of process could be used for treating wastewater with refuse activated carbon, since the carbon can be used once and discarded. An increase of $600,000 in capital costs for contact systems, engineering, etc., would raise the cost of the process from 11.6 cents to approximately 13 cents/1000 gal. This figure will serve as the capital and operating costs, exclusive of carbon and regeneration, for wastewater treatment with powdered refuse activated carbon. Although 13 cents/1000 gal is significantly higher than the 8.8 cents/1000 gal mentioned previously, the more conservative figure will be used in view of the detailed economic analysis given in reference [62]. The 13 cents/1000 gal estimate is based on a 10 MGD plant.

II. REFUSE ACTIVATED CARBON PRODUCTION SYSTEM

The refuse activated carbon production system is designed to supply slightly more than the amount of carbon required by a 10 MGD wastewater treatment plant. A 300 ton/day (ca. 25,000 lb/hr) refuse pyrolysis disposal system will produce ca. 6,800 lb/hr of pyrolysis residue which can be air classified, activated and ground to yield ca. 2,500 lb/hr of powdered activated carbon (Figure 5-1). 2,500 lb/hr of activated carbon will supply a 10 MGD wastewater treatment plant with enough carbon for a dosage of 5.95 lb/1000 gal (715 mg/1).

The dose of 715 mg/1 is computed directly from the assumptions of a 300 ton/day refuse pyrolysis disposal system and the use of the resultant

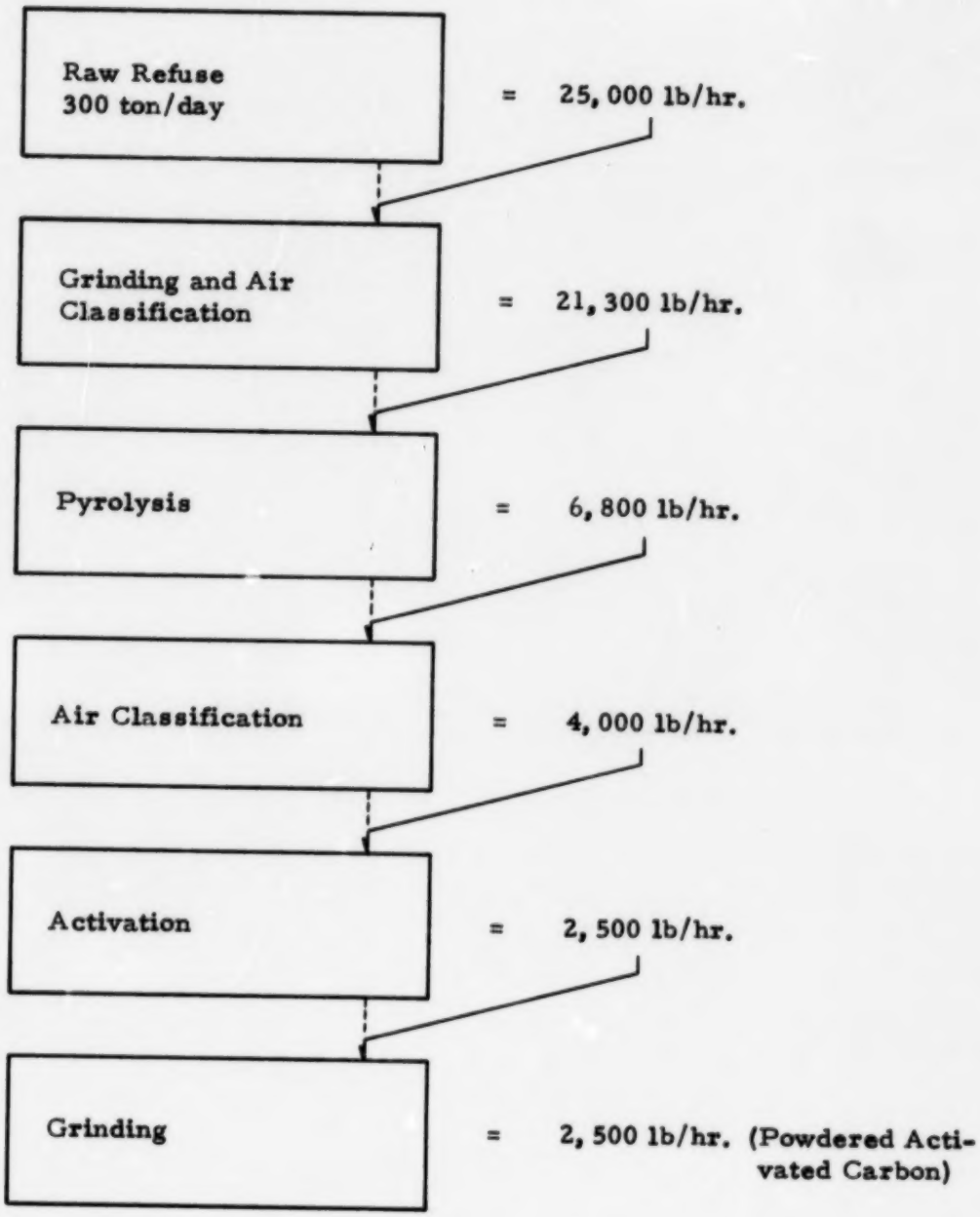

Figure 5-1. Process yields for a 300 ton/day pyrolysis and activation disposal system.

activated carbon (2,500 lb/hr) to treat 10 MGD wastewater stream. The dose of 715 mg/l is a high, conservative figure and undoubtedly can be improved upon, however, it is within the range of figures found in Table 5-1.

III. COST OF REFUSE ACTIVATED CARBON PRODUCTION SYSTEM

The economic evaluation of the carbon production system includes the installed capital and operating costs of all processes required. The installed capital and operating costs for each process are based on vendors estimates for the sizes and types of equipment needed.

A. Cost of Pyrolysis Disposal System* (25,000 lb/hr)

1. Capital Costs: $3,000,000 (@$10,000/ton-day)

   Amortization, 25 years at 6 percent

   = $234,000/year = $26.70/hr.

2. Operating Costs:

   $7.00/ton = $87.40/hr.

3. Total Cost Pyrolysis/lb Activated Carbon

   $$= \frac{11410 \text{ cents/hr}}{2500 \text{ lb/hr}} = \underline{4.57 \text{ cents/hr}}$$

B. Cost of Air Classification (6,800 lb/hr).

1. Cost Estimate Approximated from Boettcher [63] to be 40 cents/ton

   Total Hourly Cost = $1.36/hr

2. Total Cost Air Classification/lb Activated Carbon

   $$= \frac{136 \text{ cents/hr}}{2500 \text{ lb/hr}} = \underline{0.05 \text{ cents/lb}}$$

*All capital costs given are the installed capital costs. Prices are for the end of 1971. Information supplied by Monsanto-Enviro Chem, St. Louis, Missouri.

C. Cost of Activation (4,000 lb/hr of dry material in → 2,500 lb/hr out)

1. Capital Cost,* Multiple Hearth Furnace and Scrubber: $240,000.

   Amortization, 25 years at 6 percent

   = $18,800/year = 215 cents/hr.

2. Power:* (40 HP at 1 cent KW-hr).

   = 30 cents/hr

3. Fuel:*

   = 600 cents/hr

4. Maintenance:*

   (10 percent capital cost) = 25 cents/hr

5. Labor:*

   = 200 cents/hr (½ man hours)

6. Capital Cost, Control Building, Land, Utility Installation, Misc.: $50,000.

   Amortization, 25 years at 6 percent

   = $3,916/year = 45 cents/hr

7. Capital Cost,** Steam Generator, 8300 lb/hr Capacity: $45,000.

   Amortization, 25 years at 6 percent

   = $3,520/year = 40 cents/hr

8. Operating Costs,** Steam Generator:

   a. Fuel: 500 cents/hr

   b. Maintenance and chemical treatment of water:

      $300/month = 42 cents/hr

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*Cost information supplied by BSP Division, Envirotech Systems, Inc., San Francisco, California.

**Cost information supplied by Matheson and Dougherty, San Francisco, California.

9. Total Amortized Capital and Operating Costs of Activation/lb Activated Carbon:

$$\frac{1697 \text{ cents/hr}}{2500 \text{ lb/hr}} = \underline{0.68 \text{ cents/lb}}$$

D. Cost of Grinding*

1. Capital Cost, 2 each Vibrating Ball Mills, Including Replacement Parts, Maintenance: $29,000.

   Amortization, 25 years at 6 percent

   = $2,270/year = 26 cents/hr

2. Power: (30 HP at 1 cent (KW-hr).

   = 24 cents/hr

3. Total Cost Grinding/lb Activated Carbon:

$$\frac{50 \text{ cents/hr}}{2500 \text{ lb/hr}} = \underline{0.02 \text{ cents/lb}}$$

E. Engineering Design, Piping, Storage, Contingencies, etc.

1. Estimated Capital Cost: $500,000.

   Amortization, 25 years at 6 percent

   = $39,100/year = 446 cents/hr.

   Cost/hr Activated Carbon

$$= \frac{446 \text{ cents/hr}}{2500 \text{ lb/hr}} = \underline{0.18 \text{ cents/lb}}$$

F. Total Cost of Refuse Activated Carbon Production:

	Cents/lb Activated Carbon	[Without Pyrolysis] Cents/lb Activated Carbon
Pyrolysis	4.57 cents	—
Air Classification	0.05	0.05 cents
Activation	0.68	0.68
Grinding	0.02	0.02
Engineering, piping storage, contingencies, etc.	0.18	0.18
Total	5.50 cents/lb	0.93 cents/lb

*Cost information supplied by Allis Chalmers Corporation, Cement and Mining Division, San Francisco, California.

IV. COST OF WASTEWATER TREATMENT WITH REFUSE ACTIVATED CARBON

The estimated cost of wastewater treatment with refuse activated carbon is 18.5 cents/1000 gal when pyrolysis costs are not included in the carbon production costs. The carbon is assumed to be used once and discarded. The carbon dose is 715 mg/1 (5.95/1000 gal) and the carbon cost is 5.5 cents/1000 gal. The capital and operating costs are 13 cents/1000 gal. If the average estimated capital and operating costs, exclusive of make-up carbon and regeneration, given in Table 5-2 [1,2] are used, the cost of treatment may be as low as 14.3 cents/1000 gal.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER STUDY

I. CONCLUDING STATEMENT

Activated carbon produced from municipal refuse is a good adsorbent for the mixed organics in sewage. The cost of physical-chemical treatment of municipal wastewater with refuse activated carbon is estimated to be 18.5 cents per thousand gallons when the cost of pyrolysis is included in the carbon production costs and 13 cents per thousand gallons when pyrolysis costs are not included.

II. STATEMENT OF CONCLUSIONS

A. Char (pyrolysis residue) yield decreases with increasing pyrolysis temperature.

B. Char is a poor adsorbent for COD and has a correlation factor of 15.

C. Activated carbon prepared from municipal refuse is an effective adsorbent for COD, about as effective as Aqua Nuchar A.

D. Air classification of pyrolysis residue can effectively reduce the ash content of activated carbons prepared from that residue.

E. Refuse activated carbons have ash contents of 55 percent to 65 percent and do not undergo any noticeable change in apparent density on activation.

F. The yield of activated carbon from municipal refuse is approximately 10 percent for the processes used in the current study.

G. Activation of refuse chars can be achieved with air (0_2), steam, CO_2 and a steam-CO_2 mixture; the use of air requires a close control on the activation process for consistent results.

H. Oxidation of carbon with steam, during activation, is about three times as efficient at 910 C as at 800 C.

I. The properties of refuse activated carbons prepared from chars pyrolyzed at 510 C, 680 C and 910 C are similar; the methylene blue, iodine, phenol and COD adsorptive capacities of the carbons are approximately equal.

J. The adsorptive capacity of refuse activated carbons, on a unit weight of carbon basis, increases with increasing percent weight loss (during activation) when methylene blue, iodine and COD are the adsorbates; the adsorptive capacity for phenol decreases with increasing percent weight loss (greater than 20 percent).

K. The surface area of refuse activated carbons, on a unit weight of carbon basis, increases with increasing percent weight loss; the surface area of refuse activated carbons having an ash content of 55 percent to 65 percent is about 400 M_2/gm.

L. The rate of COD adsorption for ground (powdered) refuse activated carbons is similar to, but less than, the rate for Aqua Nuchar A.

M. The size of the pores of refuse activated carbons are, on the average, larger than the pores of Aqua Nuchar A.

N. Chemical catalysts, used during activation, do not markedly increase the adsorptive capacity of refuse activated carbons. Catalysts do, in general, increase the rate at which a carbon is oxidized during activation.

O. The leachates from refuse activated carbons are alkaline and result in an increase of about 2 mg/l of alkalinity and about 2 mg/l of hardness for each 100 mg/l of carbon used.

P. The treatment of waste waters with refuse activated carbon appears economical if pyrolysis costs are not included in the carbon production costs.

Q. The cost of producing activated carbon from refuse is 5.5 cents/lb; if pyrolysis costs are not included, the cost is 0.93 cents/lb. The cost of physical-chemical treatment of municipal waste water with powdered refuse activated carbon is 18.5 cents per 1,000 gallons when a carbon dose of 715 mg/l is used and when pyrolysis costs are considered in carbon production. The refuse carbon is assumed to be used once and discarded.

III. RECOMMENDATIONS FOR FURTHER STUDY

A. Determination of the total cost of treating liquid and solid wastes with an integrated system that includes consideration of the recovery of marketable refuse components.

B. A study of activation with steam at temperatures greater than 910 C. The efficiency of steam-carbon oxidation is three times greater at 910 C than at 800 C. Steam costs are significant for the activation process and might be reduced if activation temperatures higher than 910 C are used.

C. A study of methods to remove ash from refuse activated carbons. Refuse carbons with ash contents of 55 percent to 65 percent are good adsorbents for use in wastewater treatment. A reduction in ash would increase the adsorptive capacity of the carbons, per unit weight, and reduce the quantity of carbon to be activated, handled, stored, etc.

D. Determination of an effective air (O_2) activation procedure. Carbons can be activated with air at temperatures in the 300 C to 400 C range. Air can be supplied at essentially zero cost, and, at the low temperatures needed, the activation costs for refuse carbons may be much lower for air than for steam.

E. Establishment of a prototype continuous feed refuse activated carbon production system with an associated pilot plant for sewage treatment.

F. A study of the feasibility of producing granular activated carbon from refuse. Granular activated carbon may be more suitable than powdered carbon for some wastewater treatment processes; a low cost granular carbon may be produced for that purpose.

G. A study of the production of activated carbon from selected refuse components. Some refuse components are available from salvage operations which may be used as raw materials for low ash, high quality, activated carbons. H. A study of the changes that existing treatment plants can undergo for possible conversion to physical-chemical treatment with powdered refuse activated carbon.

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APPENDIX A

EXPERIMENTAL RESULTS OF ACTIVATION WITH AIR (O_2)

Carbon	Atmosphere	Temperature (°C)	Time of Activation (min.)	Percent Gross Weight Loss (%)	Ash (%)	Comments
58-A	2 ℓ/min. Air 4 ℓ/min. CO_2	350 °C	66 min.	20%	46%	
59-A	2ℓ /min. Air 4ℓ /min. CO_2	350	120	19	54	Lower than expected weight loss.
60-A	2ℓ /min. Air 3ℓ /min. CO_2	350	78	21.5	55.2	
61-A	3 ℓ/min. Air 3 ℓ/min. CO_2	350	41	28.5	-	Portion of Sample Oxidized to Ash.
62-A	2ℓ /min. Air 3ℓ /min. CO_2	350	99	36.2	-	Portion of Sample Oxidized to Ash.
63-A	2ℓ /min. Air 3ℓ /min. CO_2	350	69	26.4	49	

APPENDIX B

OPTIMUM PERCENT WEIGHT LOSS DETERMINATION FOR MAXIMIZATION OF THE METHYLENE BLUE NUMBER. IODINE NUMBER AND THE COD ADSORPTIVE CAPACITY

A. Methylene Blue Number (MB No.)

1. Determine the relationship of the MB No./unit weight carbon to percent weight loss (% W.L.) graphically from a plot similar to Figure 4-6.

   The relationship is

   $$\text{MB No./}_{\text{unit weight carbon}} = -30 + 8.0\ (\%\ \text{W.L.})$$

2. Determine the relationship of the percent ash (% ash) to the % W.L. from Figure 4-5. The relationship is

   $$\%\ \text{ash} = 30 + 0.59 \text{ percent W.L.}$$

3. Since the unit weight carbon is actually the percent carbon, the

   $$\text{Unit weight carbon} = \left(1 - \frac{\%\ \text{ash}}{100\%}\right)$$

4. Following step 3, the

   $$\text{MB No./}_{\text{unit weight carbon}} = \frac{\text{MB No. (actual)}}{1 - \frac{\%\ \text{ash}}{100\%}}$$

   therefore

   $$\text{MB No.} = \left(\text{MB No./}_{\text{unit weight carbon}}\right)\left(1 - \frac{\%\ \text{ash}}{100\%}\right)$$

5. Making the proper substitutions,

   $$\text{MB No.} = (-30 + 8.0\ \%\ \text{W.L.})\left(1 - \frac{(30 + 0.59\%\ \text{W.L.})}{100\%}\right)$$

6. Taking d MB No./d percent W.L., and setting the derivative equal to 0, the result is

   $$0 = 5.57 - 0.0944 \text{ percent W.L.}$$

7. The optimum percent W.L. = 59.2%.

B. Iodine Number (I. No.)

Using the same approach as above:

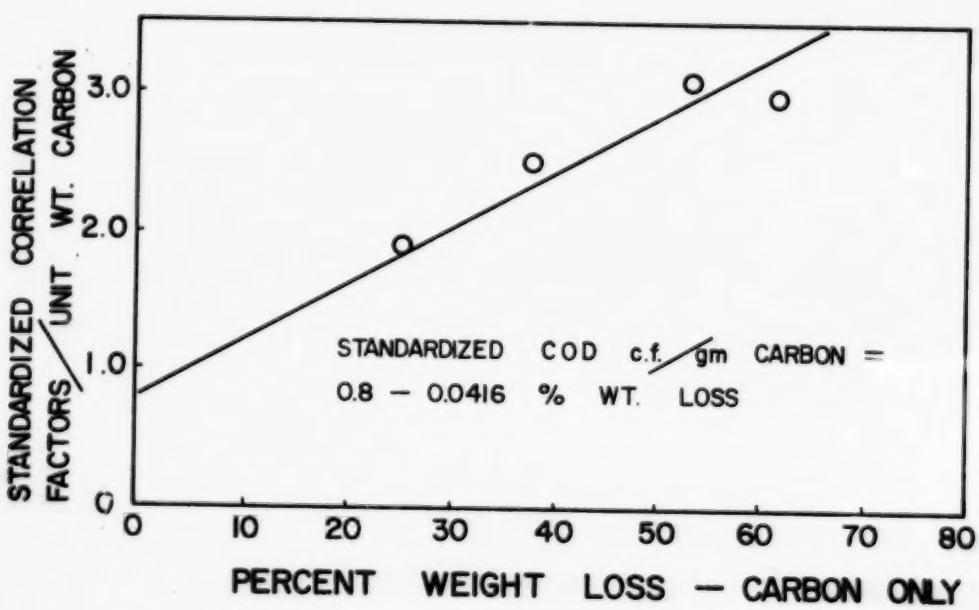
1. I. No./$_{\text{unit weight carbon}}$ = 625 + 15 percent W.L.
2. Percent ash = 30 + 0.59 percent W.L.
3. I No. = (625 + 15 percent W.L.) $\left(1 - \frac{30 + 0.59\% \text{ W.L.}}{100}\right)$
4. d I No. = 0 = 6.8 - 0.177 percent W.L.
5. The optimum percent W.L. = 38.4%.

C. COD Adsorption

1. Invert and Standardize the COD c.f. as in the table below.

Carbon	COD c.f.	Invert and Standardize the Values. Let 86-A be the Standard.	Standardized Values Per Unit Weight of Carbon
85-A	1.12	1.03	1.87
Steam	0.95	1.21	2.50
88-A	0.96	1.20	3.08
86-A	1.15	1.00	2.98

2. Plot the standardized correlation factors/per unit weight of carbon (Std. c.f./$_{C}$) as a function of the percent W.L., as shown below).



3. Determine the relationship of Std. c.f./$_C$ to % W.L. from the figure above.

$$\text{Std. c.f.}/_C = 0.8 + 0.0416\% \text{ W.L.}$$

4. $\%$ ash $= 30 + 0.59\%$ W.L.

5. $$\text{Std. c.f.}/_C = \frac{\text{Std. c.f.}}{1 - \frac{\% \text{ ash}}{100\%}}$$

6. $$\text{Std. c.f.} = (0.8 + 0.0416\% \text{ W.L.}) \left(1 - \frac{(30 + 0.59\% \text{ W.L.})}{100\%}\right)$$

7. $$\frac{d \text{ Std. c.f.}}{d \% \text{ W.L.}} = 0 = 2.44 - 0.0492\% \text{ W.L.}$$

8. The optimum % W.L. = <u>49.6%</u>.

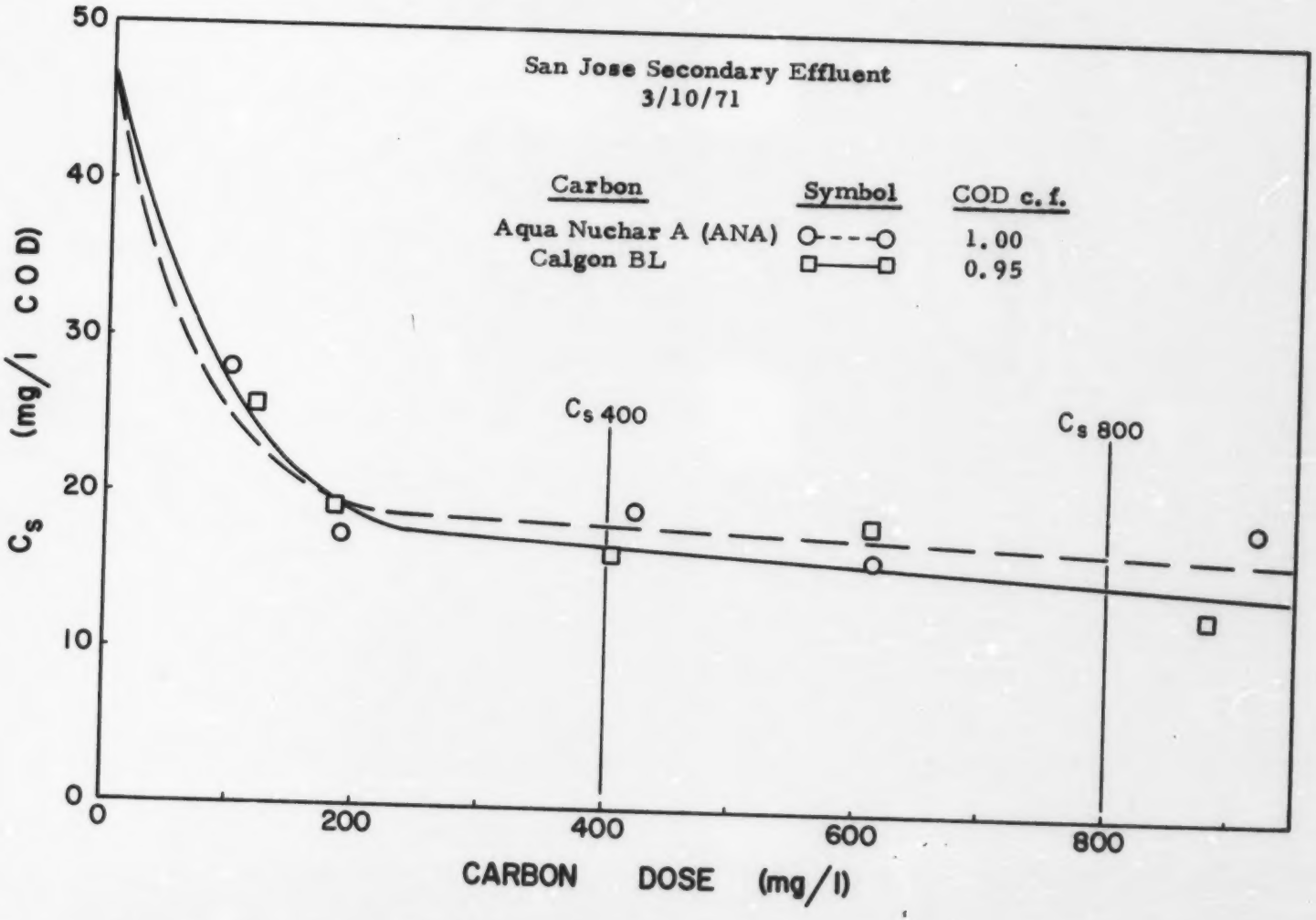
APPENDIX C

CALCULATION OF COD CORRELATION FACTORS FOR REFUSE ACTIVATED CARBONS

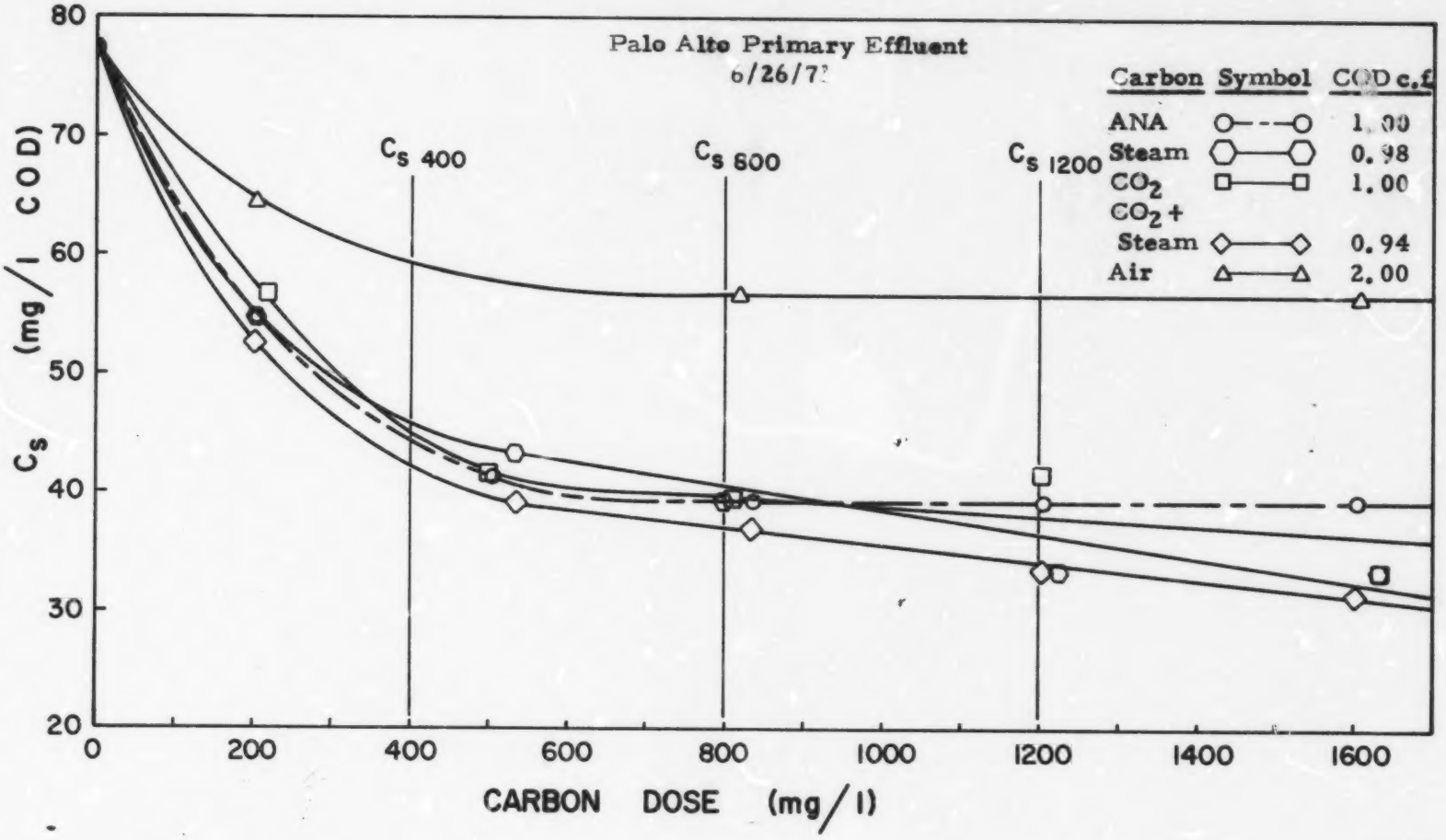
Appendix, Sewage, Date, C_o (mg/l COD)	Carbon	C_s 400	$C_o - C_s$	c.f.	C_s 800	$C_o - C_s$	c.f.	C_s 1200	$C_o - C_s$	c.f.	Average c.f.
3-A, San Jose Secondary, 3/10/71, C_o = 46.4	Aqua Nuchar A (ANA)	18.2	28.2	1.00	17.1	29.3	1.00	-	-	-	1.00
	Calgon BL	16.9	29.5	0.96	15.1	31.3	0.94	-	-	-	0.95
3-B, Palo Alto Primary, 6/26/71, C_o = 76	ANA	43	33	1.00	39	37	1.00	39	37	1.00	1.00
	Steam	43	33	1.00	39	37	1.00	36	40	.98	.98
	CO_2	45	31	1.06	39	37	1.00	37	39	1.00	1.00
	CO_2 + Steam	42	34	.97	38	38	0.97	34	42	.94	0.94
	Air	60	16	2.06	57	19	1.95	57	19	2.00	2.00
3-C, Palo Alto Primary, 6/28/71, C_o = 65	ANA	40	25	1.00	35	30	1.00	34	31	1.00	1.00
	Steam	34	31	0.81	26	39	.77	22	43	.72	0.77
	CO_2	37	28	0.89	30	35	.86	26	39	.80	0.85
	CO_2 + Steam	36	29	0.86	29	36	.83	25	40	.78	0.82
3-D, San Jose Secondary, 7/1/71, C_o = 38	ANA	22	16	1.00	17	21	1.00	14	24	1.00	1.00
	Steam	22	16	1.00	16	22	.95	12	26	0.92	0.96
	CO_2	22	16	1.00	16	22	.96	13	25	0.96	0.97
	CO_2 + Steam	22	16	1.00	17	21	1.00	14	24	1.00	1.00
3-E, Palo Alto Primary, 7/22/71, C_o = 75	ANA	44	31	1.00	40	35	1.00	36	39	1.00	1.00
	71-A	53	22	1.41	42	33	1.06	33	42	0.93	1.13
	86-A	48	27	1.15	44	31	1.13	42	33	1.18	1.15
	88-A	46	29	1.07	38	37	0.95	30	45	0.87	0.96
	89 + 90-A	46	29	1.07	35	40	0.87	27	48	0.81	0.92
	91 + 92-A	49	26	1.19	38	37	0.95	31	44	0.89	1.01

APPENDIX C (Continued)

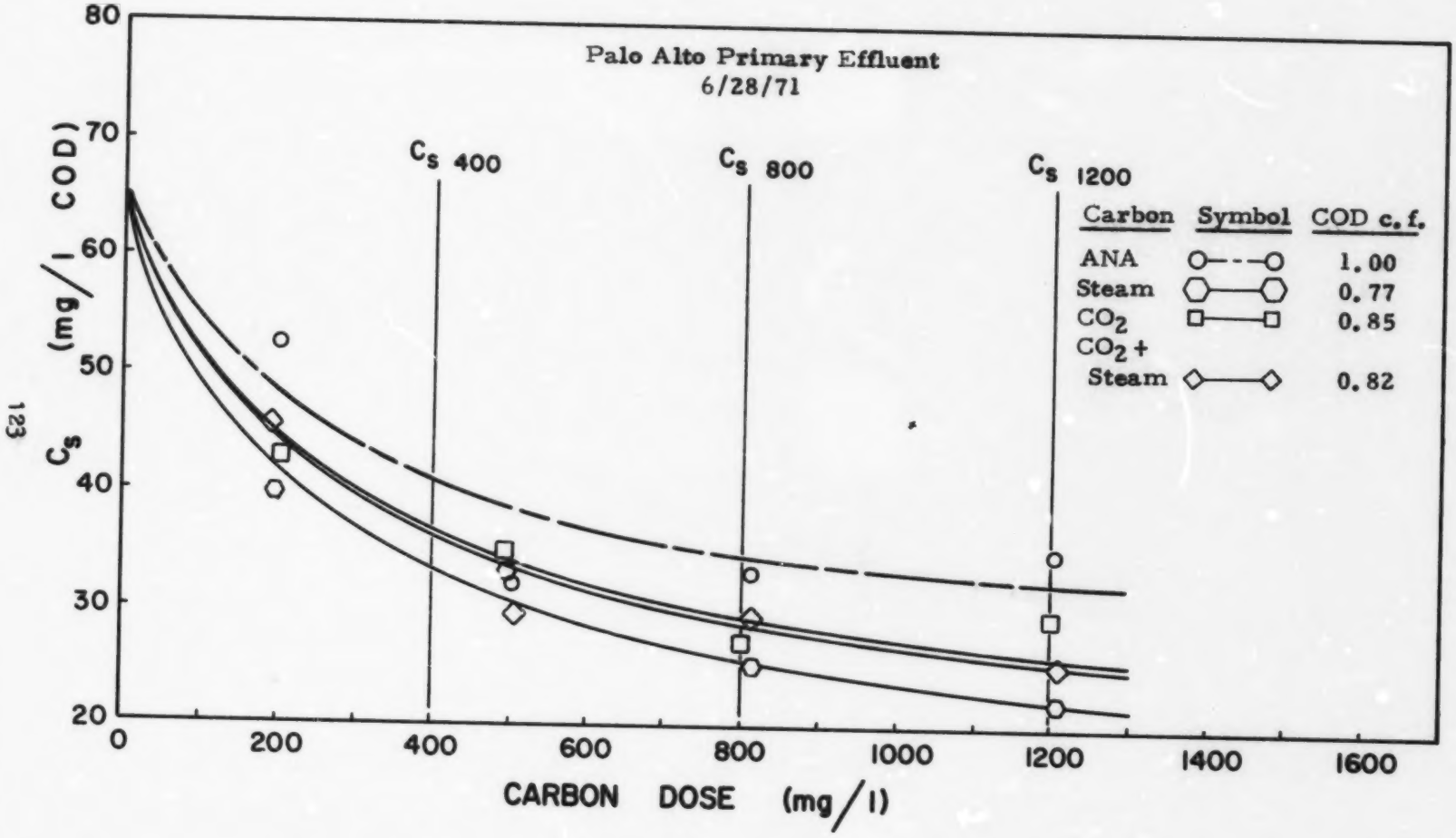
Appendix, Sewage, Date, C_o (mg/l COD)	Carbon	C_s 400	$C_o - C_s$	c.f.	C_s 800	$C_o - C_s$	c.f.	C_s 1200	$C_o - C_s$	c.f.	Average c.f.
3-F, Palo Alto	ANA	46	29	1.00	43	32	1.00	40	35	1.00	1.00
Primary,	83-A	51	24	1.21	46	29	1.10	42	33	1.06	1.12
8/23/71,	85-A	51	24	1.21	46	29	1.10	42	33	1.06	1.12
C_o = 75	Steam	44	31	0.93	40	35	0.91	39	36	0.97	0.94
	CO_2	51	24	1.21	46	29	1.10	44	31	1.13	1.15
	CO_2 + Steam	46	29	1.00	43	32	1.00	40	35	1.00	1.00
3-G, Palo Alto	ANA	48	33	1.00	44	37	1.00	41	40	1.00	1.00
Primary,	Darco M	48	33	1.00	44	37	1.00	41	40	1.00	1.00
9/1/71,	85-A	56	25	1.32	50	31	1.19	46	35	1.14	1,22
C_o = 81	Steam	53	28	1.18	46	35	1.06	42	39	1.02	1.09
	CO_2	47	34	0.97	42	39	0.95	39	42	0.95	0.96
3-H, Palo Alto	ANA	2.15	2.05	1.00	1.65	2.55	1.00	1.50	2.70	1.00	TOC c.f. 1.00
Primary,	Darco M	1.80	2.40	0.85	1.50	2.70	0.95	1.45	2.75	0.98	0.93
9/1/71,	Steam	2.30	1.90	1.08	1.70	2.50	1.02	1.45	2.75	0.98	1.03
C_o=4.2 mg.l TOC.	CO_2	2.10	2.10	0.98	1.50	2.70	0.95	1.30	2.90	0.93	0.95
	85-A	2.65	1.55	1.32	1.95	2.25	1.13	1.70	2.50	1.08	1.18
3-I, 3-J, 3-K,	ANA	46	24	1.00	45	25	1.00	45	25	1.00	1.00
Palo Alto	93-4	54	16	1.50	44	26	0.96	37	33	0.76	1.07
Primary,	94-A	49	21	1.14	39	31	0.81	36	34	0.74	0.90
9/25/71,	96-A	45	25	0.96	41	29	0.86	39	31	0.81	0.88
C_o = 70											
	ANA	46	24	1.00	45	25	1.00	45	25	1.00	1.00
	95-A	47	23	1.04	44	26	0.96	43	27	0.93	0.98
	97-A	48	22	1.09	43	27	0.93	41	29	0.86	0.96
	98-A	42	28	0.86	38	32	0.78	37	33	0.76	0.80
	ANA	46	24	1.00	45	25	1.00	45	25	1.00	1.00
	99-A	44	26	0.92	40	30	0.83	40	30	0.83	0.86
	101-A	45	25	0.96	38	32	0.78	35	35	0.72	0.82
	100-A	42	28	0.86	41	39	0.86	41	29	0.86	0.86



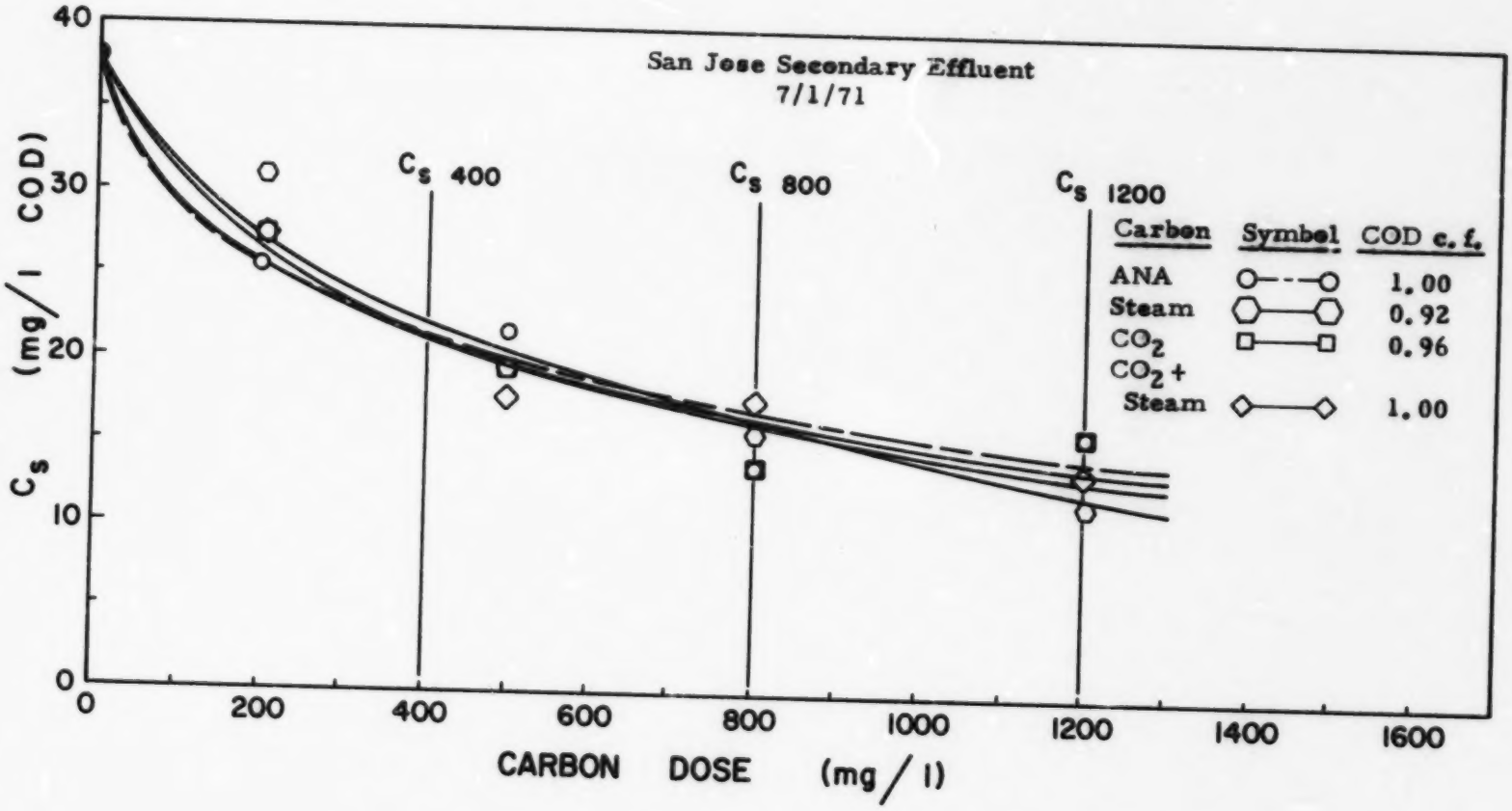
Appendix C-3. COD ADSORPTION STUDY. COD concentration as a function of carbon dose.



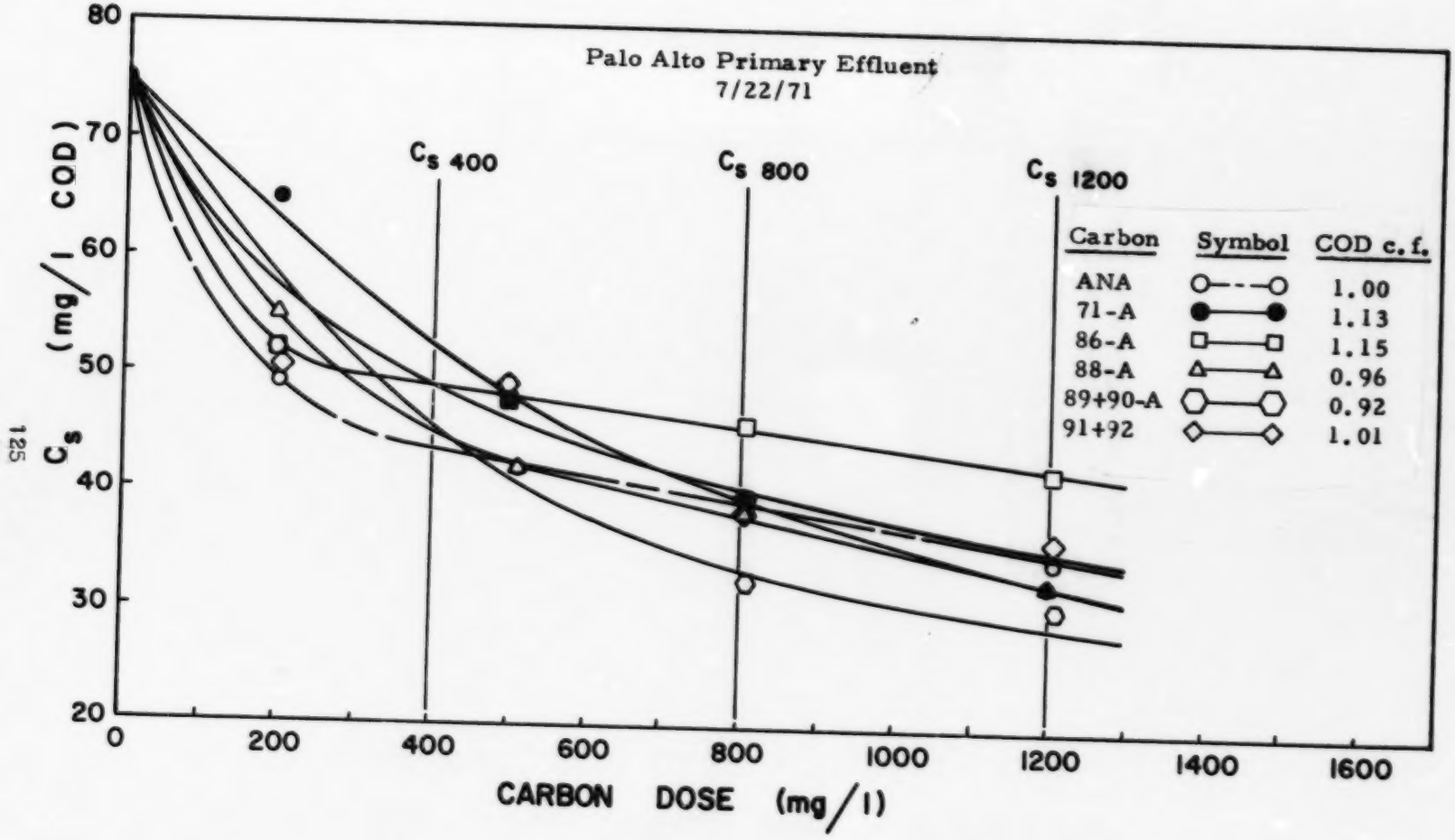
Appendix C-4. COD ADSORPTION STUDY. COD **concentration as a function of carbon dose.**



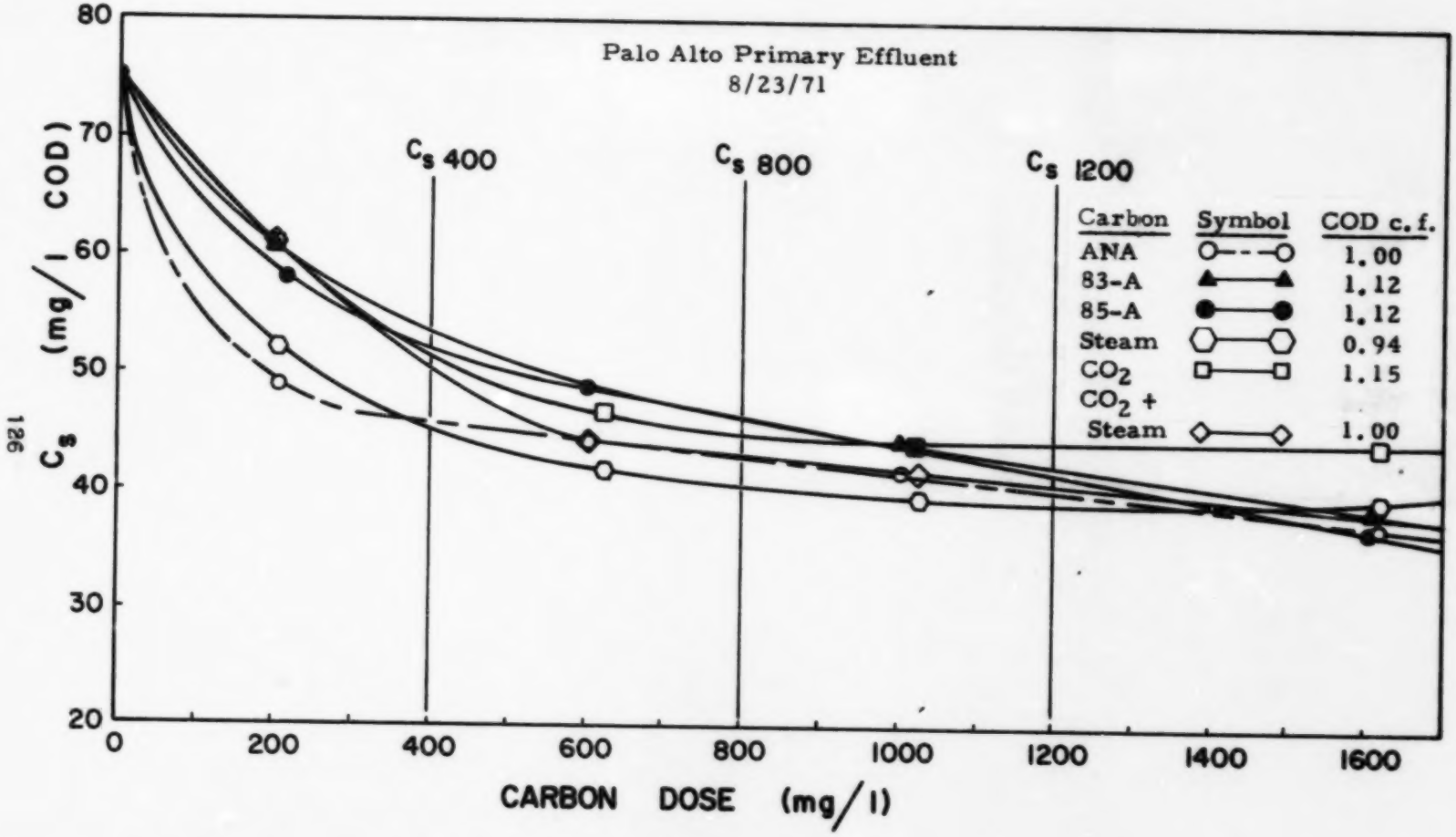
Appendix C-5. COD ADSORPTION STUDY. COD concentration as a function of carbon dose.



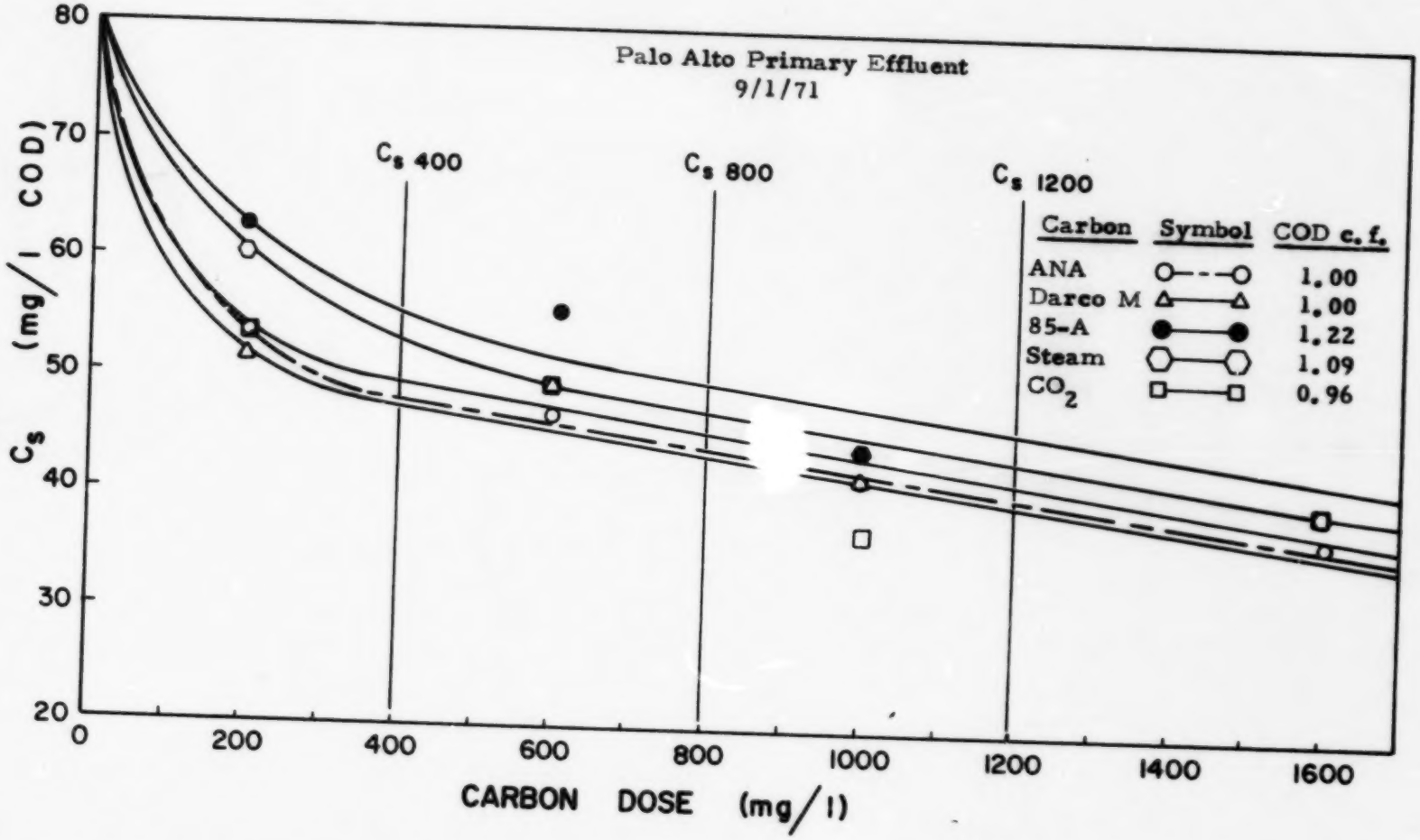
Appendix C-6. COD ADSORPTION STUDY. COD concentration as a function of carbon dose.



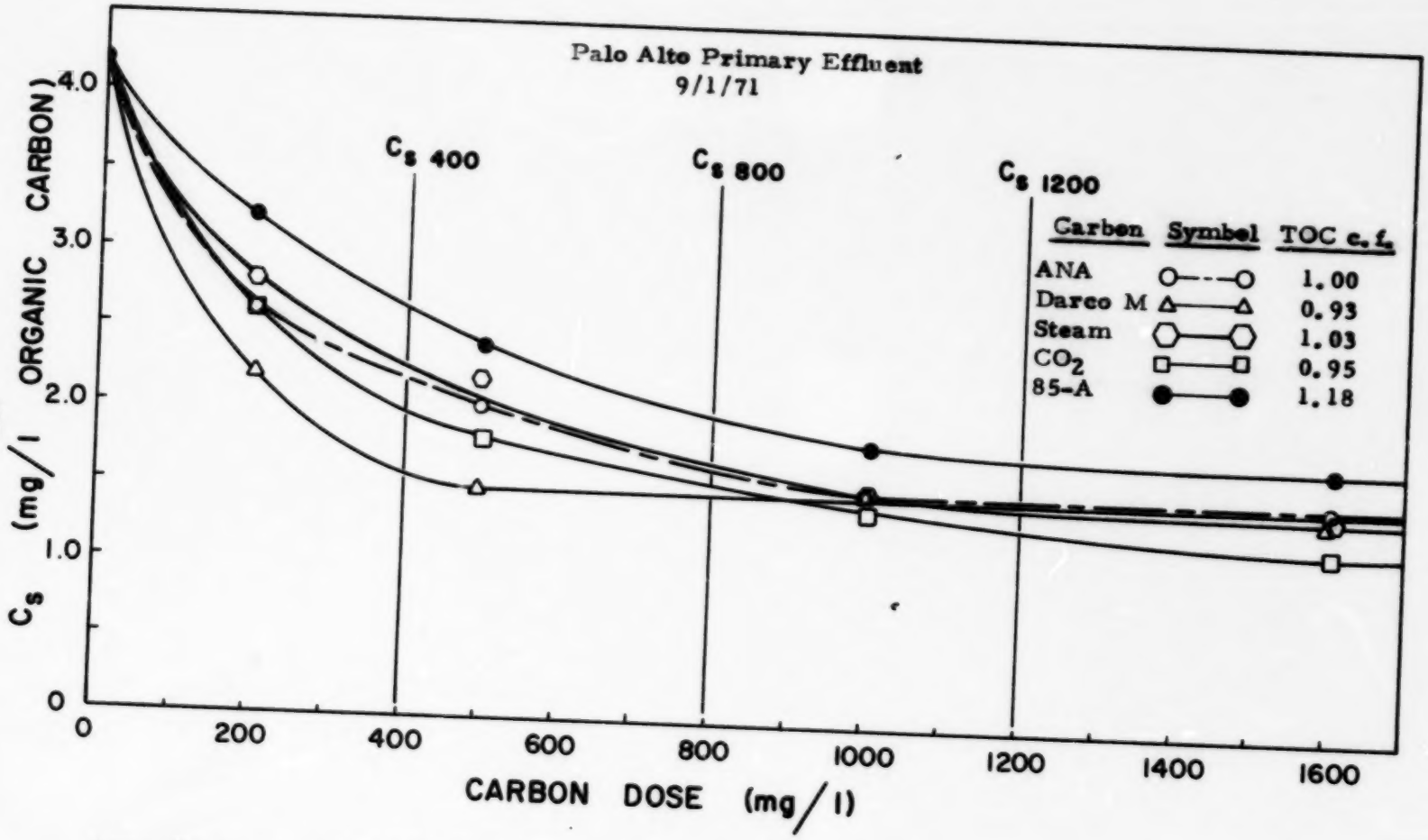
Appendix C-7. COD ADSORPTION STUDY. COD concentration as a function of carbon dose.



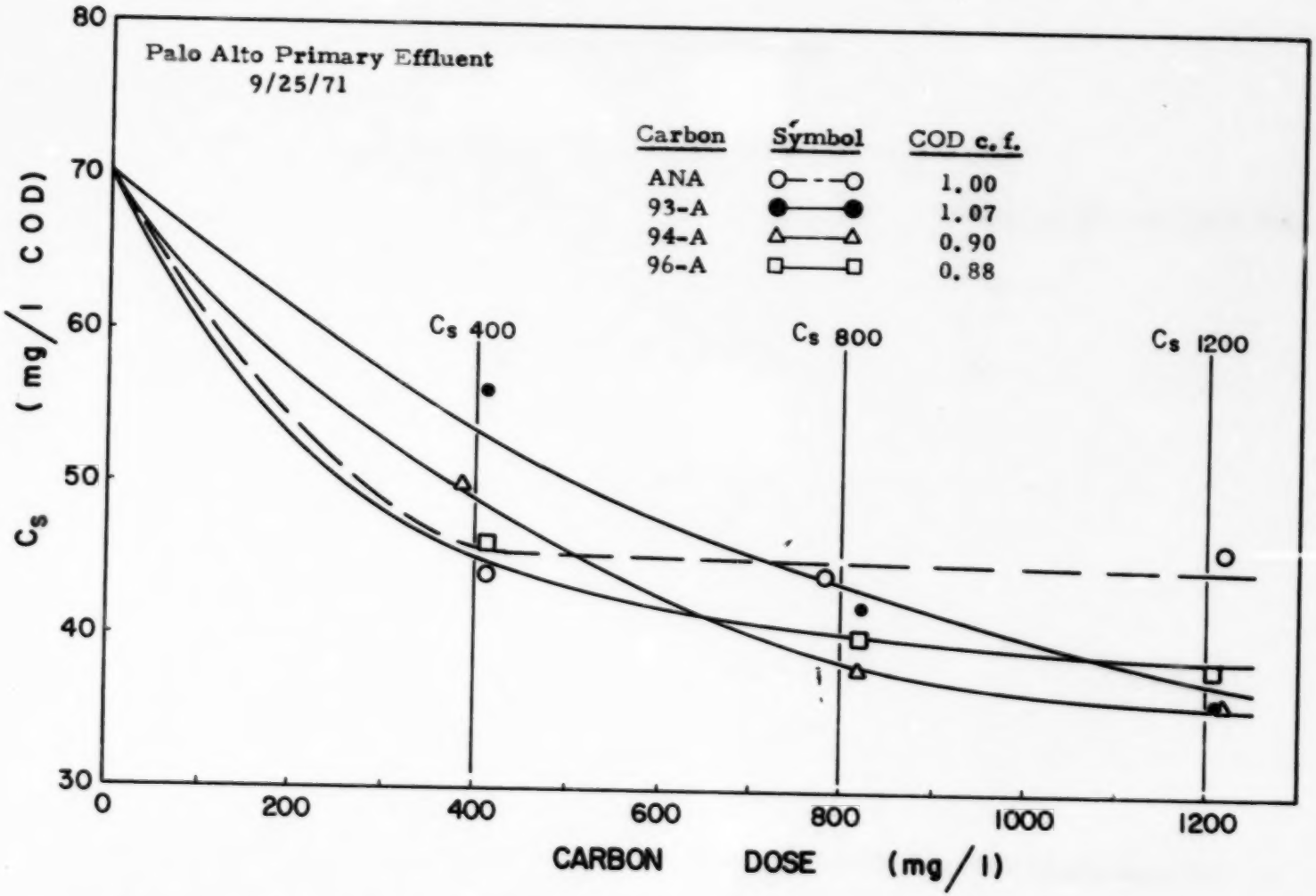
Appendix C-8. COD ADSORPTION STUDY. COD **concentration as a function of carbon dose.**



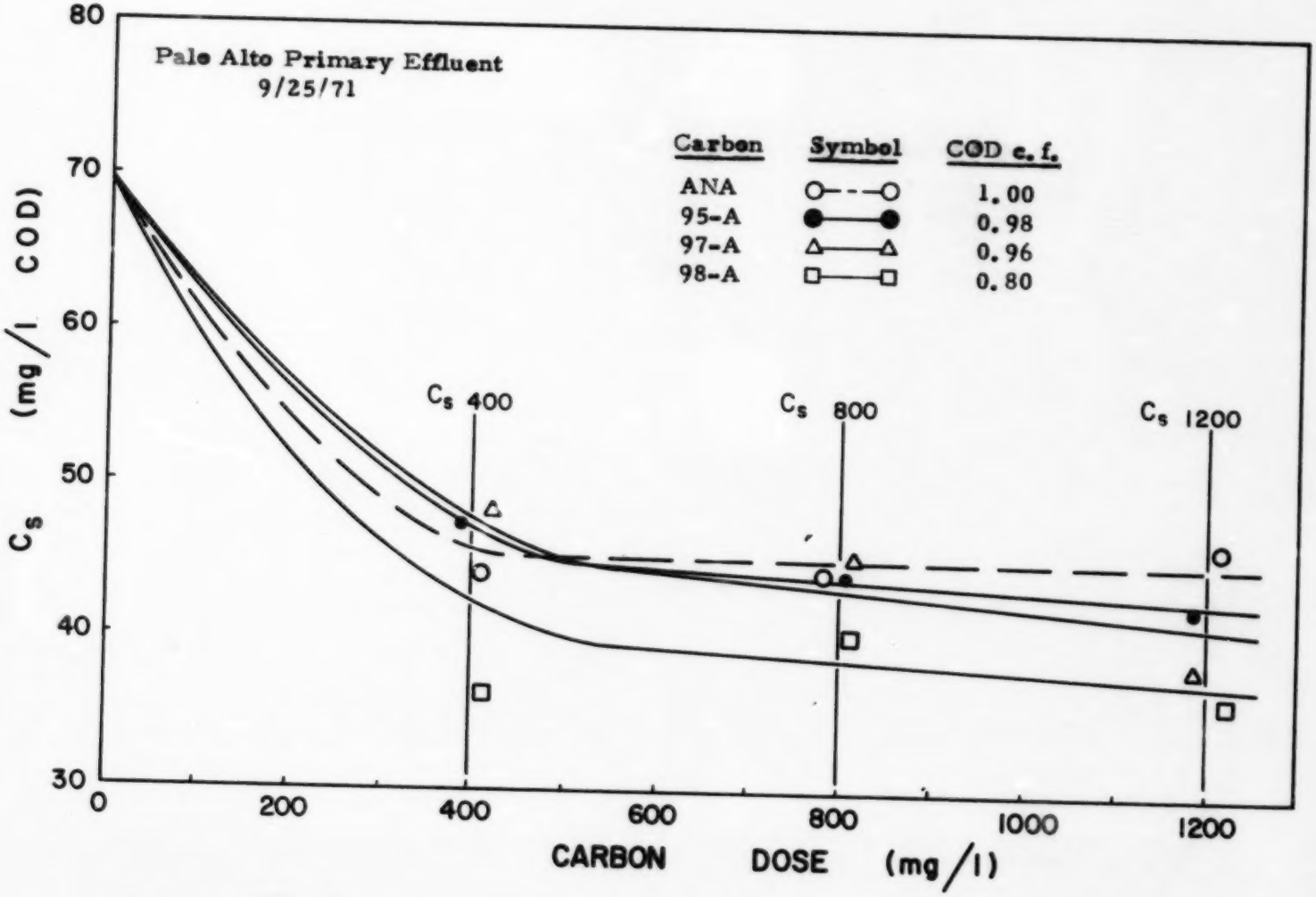
Appendix C-9. COD ADSORPTION STUDY. COD concentration as a function of carbon dose.



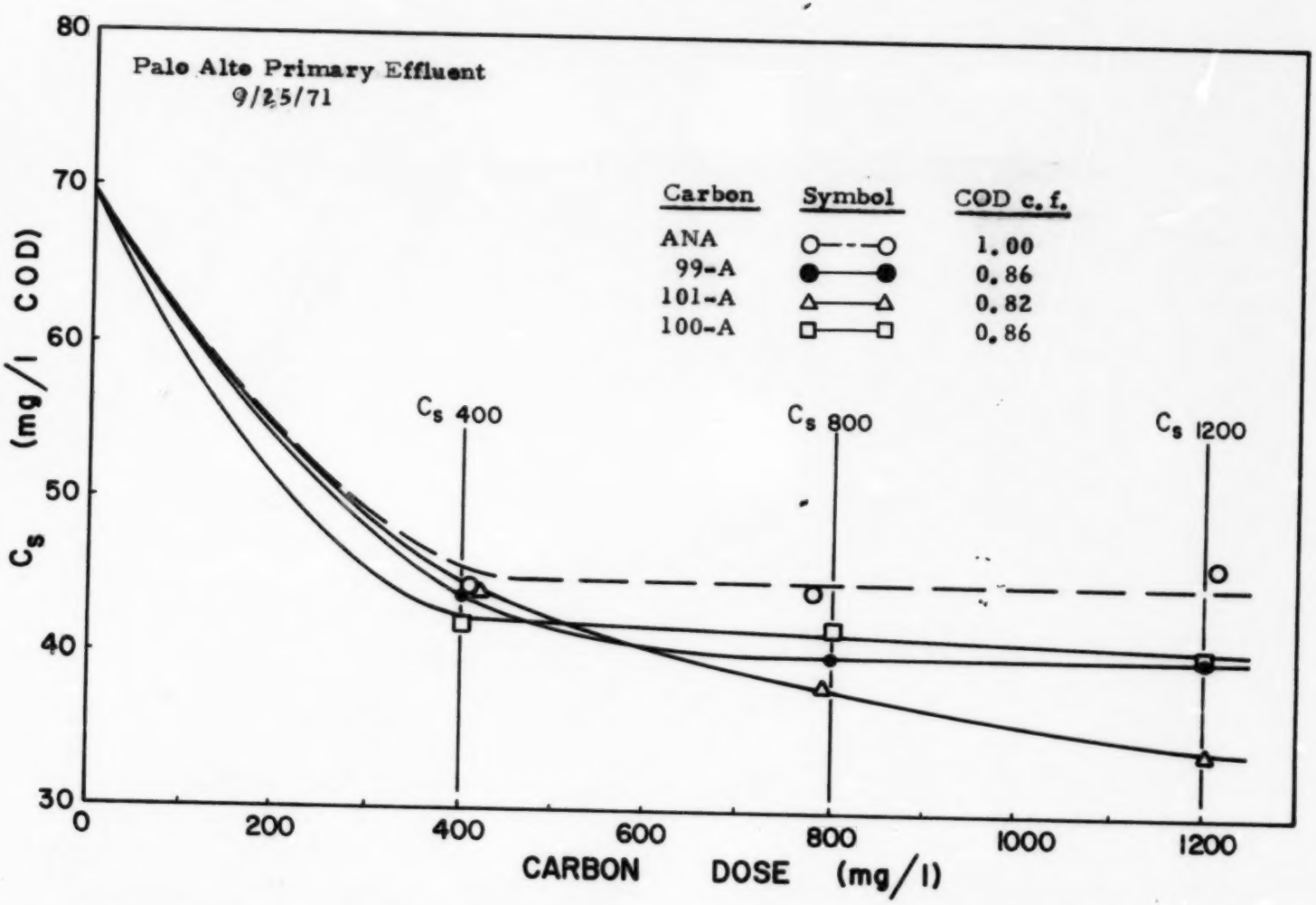
Appendix C-10. TOC ADSORPTION STUDY. TOC concentration as a function of carbon dose.



Appendix C-11. COD ADSORPTION STUDY. COD concentration as a function of carbon dose.



Appendix C-12. COD ADSORPTION STUDY. COD concentration as a function of carbon dose.

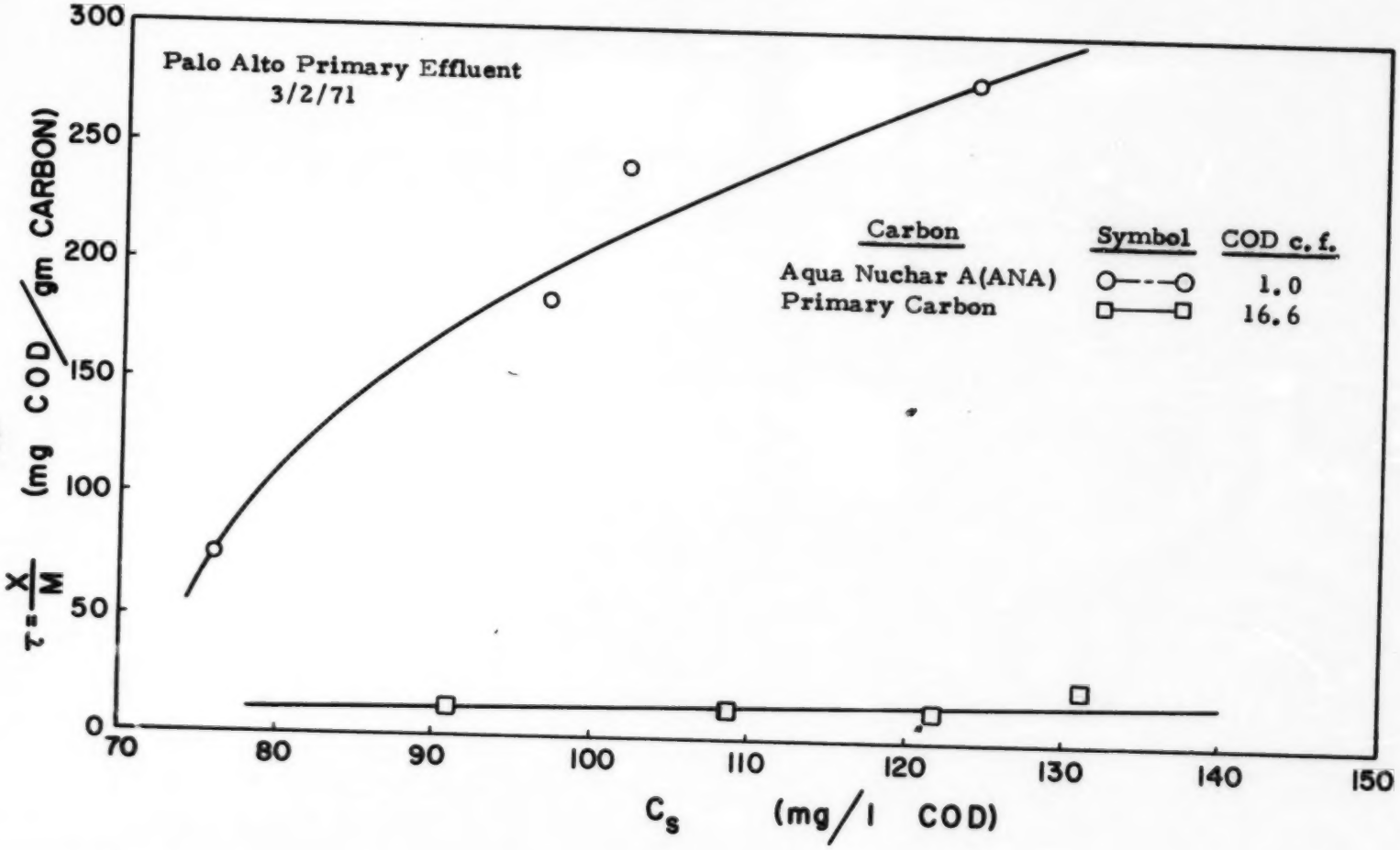


Appendix C-13. COD ADSORPTION STUDY. COD concentration as a function of carbon dose.

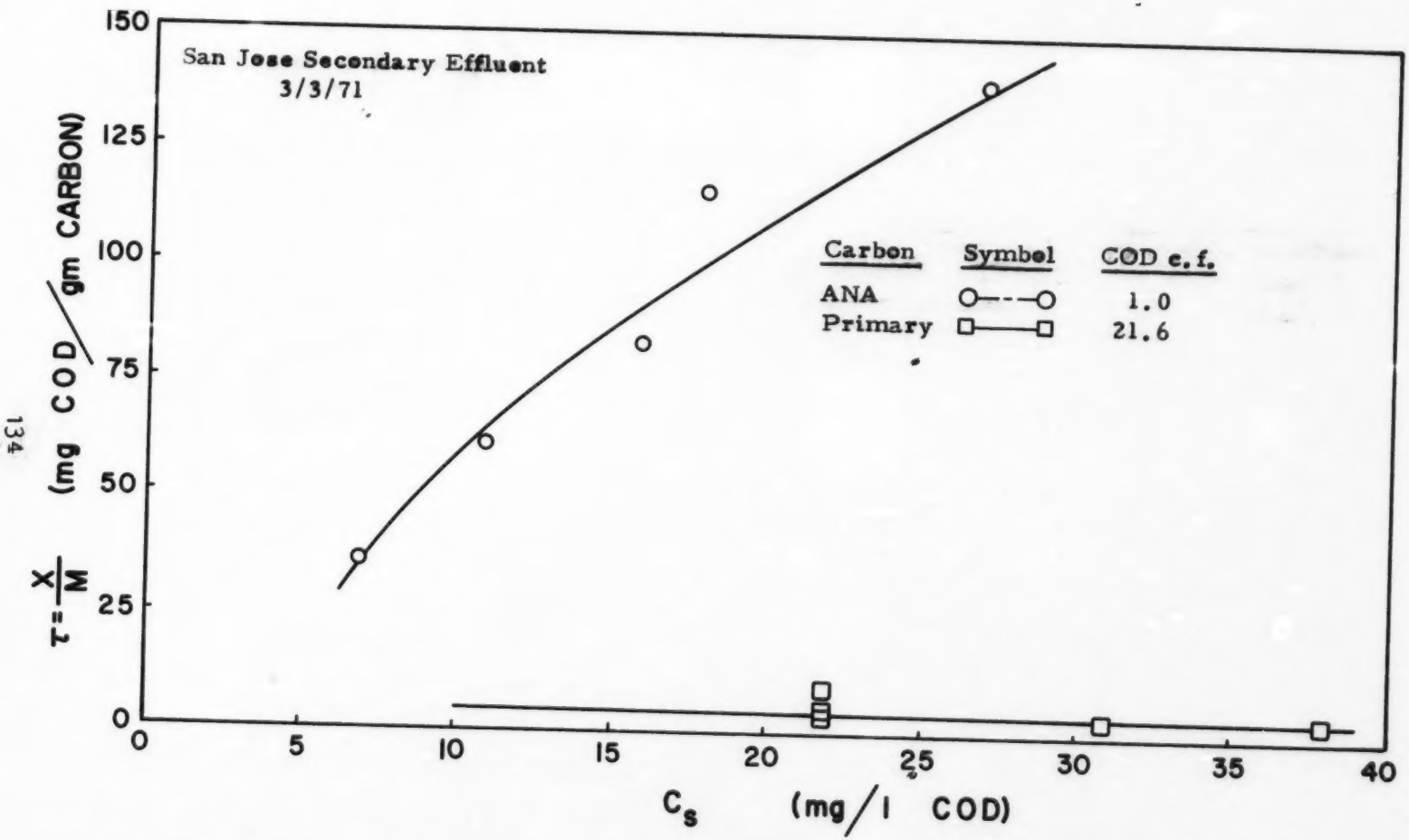
APPENDIX D

CALCULATION OF COD CORRELATION FACTORS FOR PRIMARY CARBON

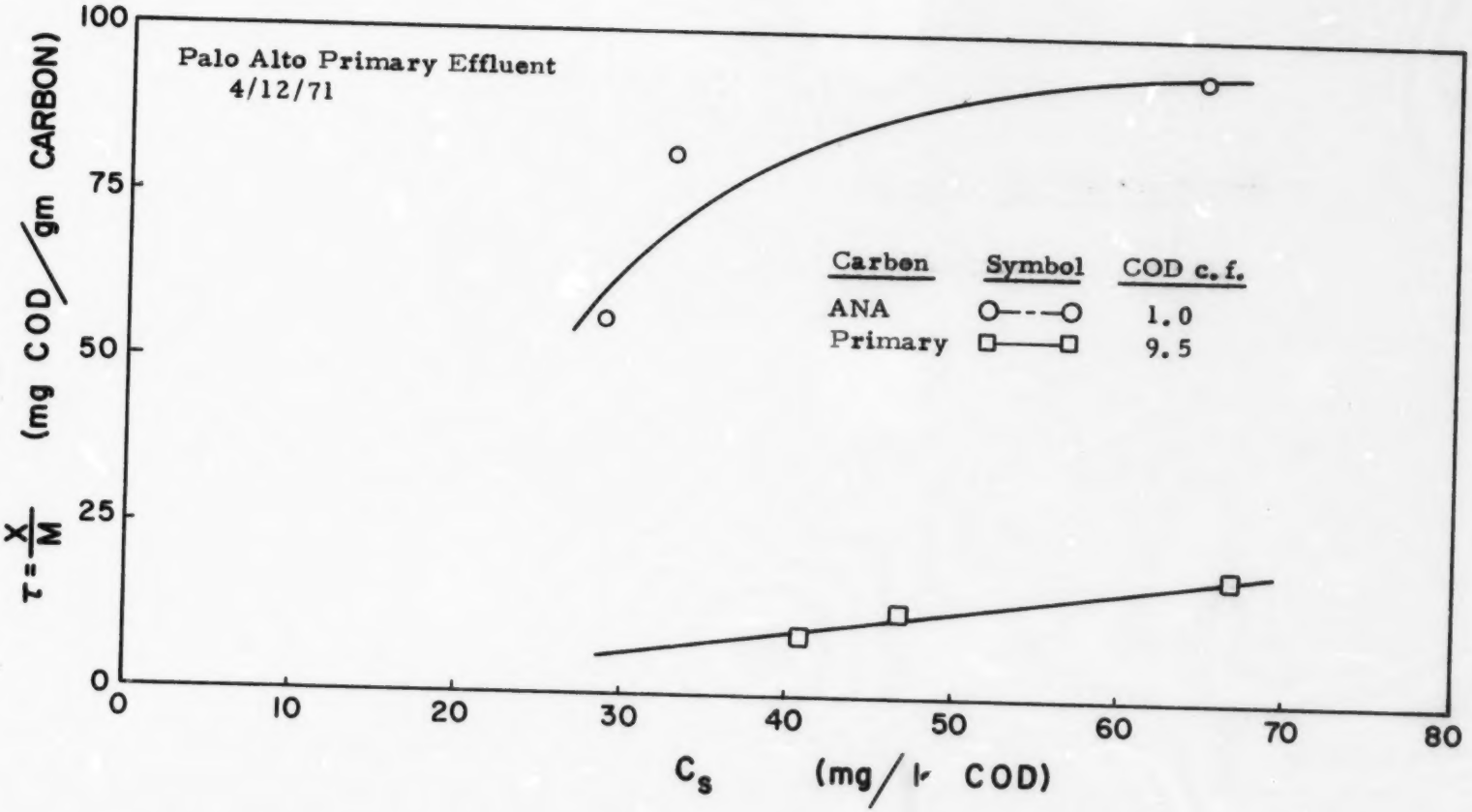
Appendix, Sewage, Date, C_o (mg/l COD)	Carbon	τ_{C_s}=95	c.f.	τ_{105}	c.f.	τ_{115}	c.f.	Average COD c.f.
4-A, Palo Alto Primary, 3/2/71, C_o=153	Aqua Nuchar A (ANA)	185	1.0	220	1.0	250	1.0	1.0
	Primary	12	15.5	14	15.7	15	16.6	15.9
		τ_{C_s}=10	c.f.	τ_{15}	c.f.	τ_{20}	c.f.	
4-B, San Jose Secondary, 3/3/71, C_o=41	ANA	65	1.0	85	1.0	108	1.0	1.0
	Primary	5	13.0	5	17.0	5	21.6	17.2
		τ_{C_s}=30	c.f.	τ_{40}	c.f.	τ_{50}	c.f.	
4-C, Palo Alto Primary, 4/12/71, C_o =84	ANA	65	1.0	84	1.0	91	1.0	1.0
	Primary	6	10.8	9	9.3	11	8.3	9.5
		τ_{C_s}=30	c.f.	τ_{40}	c.f.	τ_{50}	c.f.	
4-D, Palo Alto Primary, 2/27/71 C_o=69	ANA	150	1.0	200	1.0	250	1.0	1.0
	Primary	9	16.6	10	20.0	13	19.2	18.6



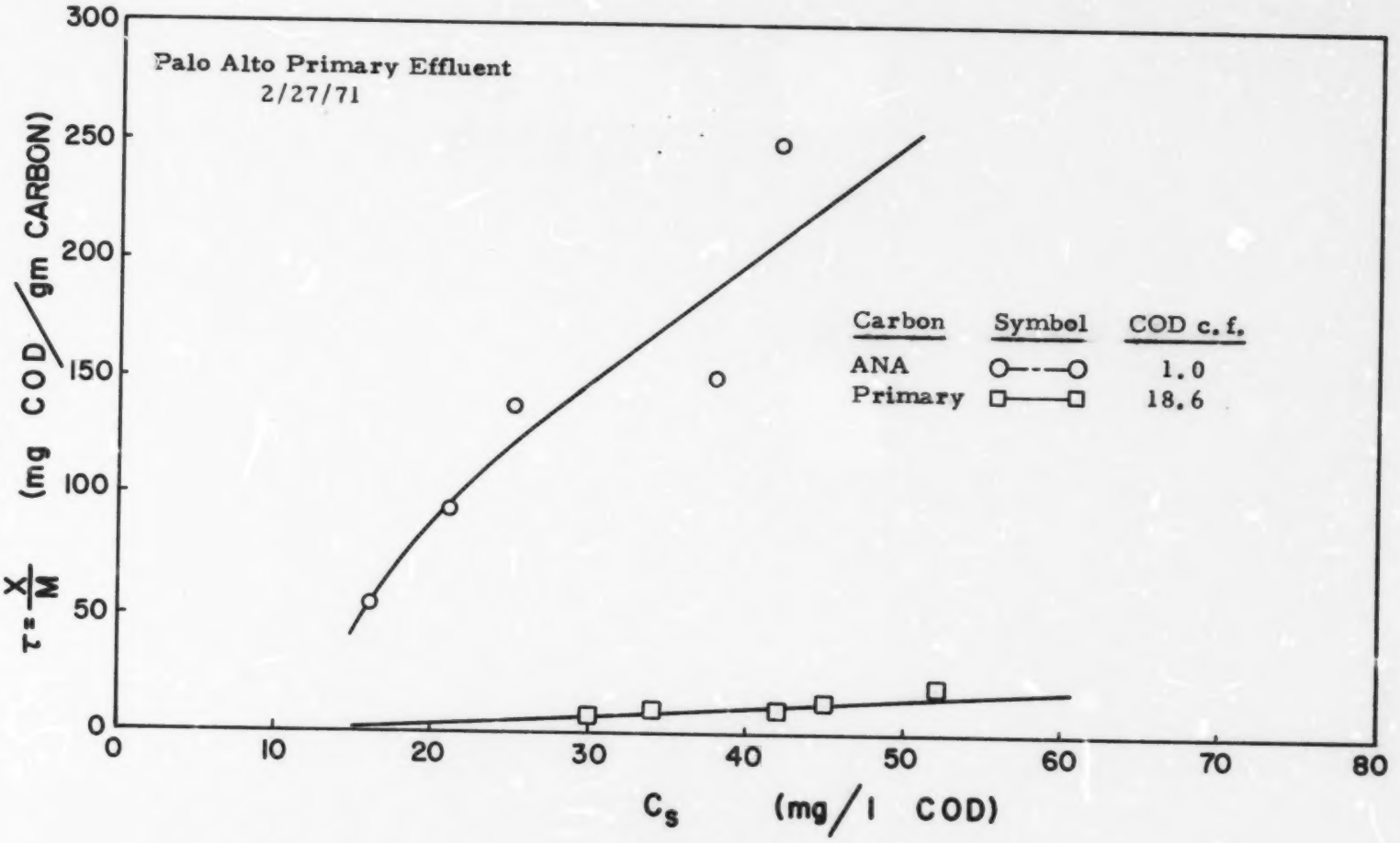
Appendix D-2. COD ADSORPTION STUDY. COD adsorbed per unit weight of adsorbent as a function of COD concentration.



Appendix B-3. COD ADSORPTION STUDY. COD adsorbed per unit weight of adsorbent as a function of COD concentration.



Appendix D-4. COD ADSORPTION STUDY. COD adsorbed per unit weight of adsorbent as a function of COD concentration.



Appendix D-5. COD ADSORPTION STUDY. COD adsorbed per unit weight of adsorbent as a function of COD concentration.